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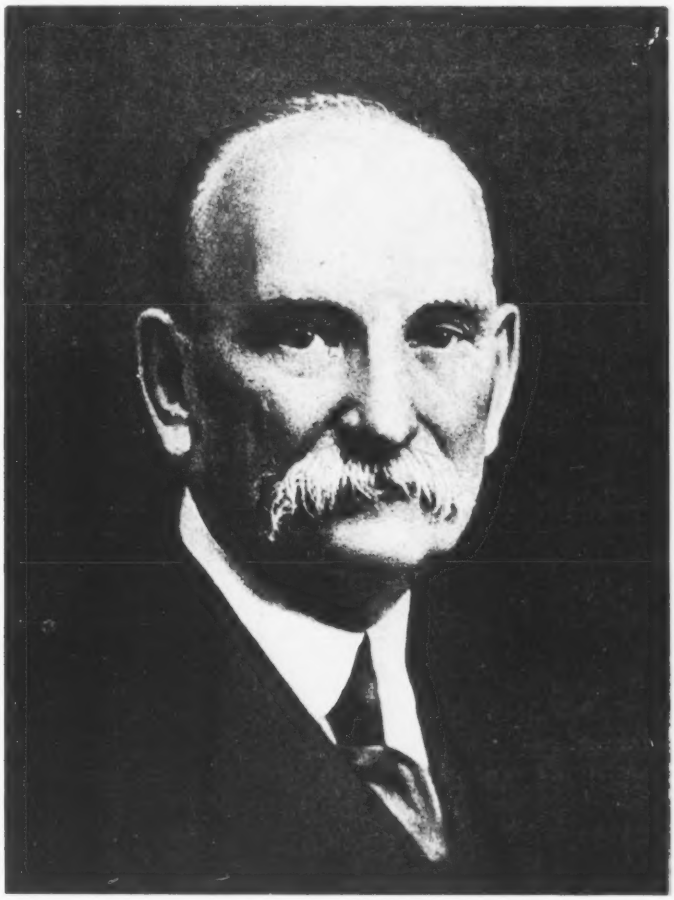
N. S. KURNAKOV

(ON THE CENTENARY OF HIS BIRTH)

Yu. I. Solov'ev

Translated from Zhurnal Strukturnoi Khimii, Vol. 1, No. 4, pp. 395-398, November-December, 1960

Nikolai Semenovich Kurnakov, an eminent chemist of the end of the past, and the first half of the present century, graduated from the Mining Institute in Petersburg in the spring of 1882 with the degree of mining engineer. He was then 22 years of age.*



*N. S. Kurnakov was born November 24, 1860 in Nolinsk (former Vyatka province). Fuller information on the life and the scientific, teaching, and social activities of Academician N. S. Kurnakov is given in the book by Yu. I. Solov'ev and A. E. Zvyagintsev: Nikolai Semenovich Kurnakov, His Life and Activity [in Russian] (Izd. AN SSSR, Moscow, 1960).

Having received excellent training in chemistry, metallurgy, mineralogy, and mining from such professors as K. I. Lisenko, A. P. Karpinskii, P. V. Eremeev, and N. A. Ioss, Kurnakov achieved very significant results in the very first years of his independent scientific work. His interests were initially directed toward problems in chemical technology. He studied metal smelting processes in Altai factories, and in 1885 presented, at the Mining Institute, a dissertation entitled Evaporation Systems in Salt Pans in connection with his application for the title of Assistant in the Department of Metallurgy, Halurgy, and Assaying.

In the 1890's, Kurnakov worked in a different field – research on the chemistry of complex compounds. The results of his very interesting work (he discovered the reaction of cis- and trans-isomers of bivalent platinum with thiourea) were presented in the dissertation, Complex Metallic Bases, for which he was awarded the title of Professor in the Department of Chemistry in 1894.

Full of vigor and ambition, the young professor understood, before many Russian and European scientists, what wealth is hidden in physicochemical studies of the nature of metallic and other complex systems. The intensive development of the metallurgical industry demanded a knowledge of complex heterogeneous equilibria in alloys. By 1880-1890, physical chemistry had already made some notable advances: chemical thermodynamics had been developed, including the theory of phases (Gibbs) and of chemical equilibria (Van't Hoff, Le Chatelier). It proved possible to extend the basic laws (those of Raoult and Van't Hoff) established for aqueous solutions, to the field of metallic alloys. The invention of the thermocouple by Le Chatelier in 1887 must be mentioned. All this made it possible to study the nature of alloys and other systems from all aspects.

Since 1899, when N. S. Kurnakov's paper, "Intermetallic compounds" was published, he and his numerous associates (S. F. Zhemchuzhnyi, N. I. Stepanov, and others) carried out systematic studies of various metallic, salt, and organic systems over a period of many years, first in the Mining Institute and subsequently in the Petersburg Polytechnic Institute. It is not possible to consider here the actual results obtained in these studies, but it must be emphasized that the extensive experimental investigations of phase equilibria and numerous studies of such physicochemical properties as electrical conductivity, hardness, internal friction, etc., apart from their enormous practical importance, enabled Kurnakov to formulate outstanding theoretical generalizations.

During 1900-1914, Kurnakov did an enormous amount of work on analysis of experimental data. The Archives of the Academy of Sciences contain an interesting letter (1912) from Kurnakov to one of his outstanding pupils, N. I. Stepanov, in which he wrote: "I personally spent thissummer very usefully and productively. I had to do much writing, thinking, and reading, to obtain deeper insight into the discoveries made in our laboratory during recent years. I came to the conclusion that in the place which we occupy with our research in the scientific field, we must work unceasingly so as to make the best use of the favorable conditions offered by the new and unexplored fields.

"Electrical conductivity of metallic alloys, hardness, and other closely associated mechanical properties – these are our scientific conquests which we must hold. We need planned and systematic work by a large number of conscientious and independent workers.

"Even such scientists as Tammann have not recognized the significance of the electrical conductivity method for investigation of the nature of metallic alloys (read the discussion on Guertler's paper at the last conference of the Bunsen Society in Heidelberg, reported in Z. f. Elektrochem.). Here I can only say: so much the better for us – we are ahead."*

In 1913, N. S. Kurnakov and S. F. Zhemchuzhnyi wrote: "Joint and continuous theoretical and experimental work opens up before us a new boundary region of chemical knowledge, where the aim is to determine the chemical nature of uni- and multicomponent systems on the basis of studies of the relationships between composition and physicochemical properties. This region may be given the name of physicochemical analysis.

In Kurnakov's words, "The main task of physicochemical analysis is measurement of properties during progressive changes in the composition of an equilibrium system, leading to the construction of a 'composition–property' diagram. Thus we have a geometrical method for investigating chemical changes. We obtain an exact

* Archives of the Academy of Sciences USSR, F. 321, Op. 1, No. 63.

** N. S. Kurnakov, Selected Works [in Russian] (ONTI, Leningrad, 1938) Vol. 1, p. 384.

geometrical model of the complex function which should represent the relationship between temperature, volume, concentration, and other physical and chemical factors determining the state of the system."

On January 2, 1914, N. S. Kurnakov gave a paper to the chemistry section of the First All-Russian Congress of Teachers of Physics, Chemistry, and Cosmography, on the subject of "Compounds and chemical species," in which he summarized many years of work on physicochemical analysis of metallic alloys, and presented the general theoretical conclusions drawn from this work.

In this paper, Kurnakov defined the concepts of chemical species and phase. "In reality," he said, "the direct initial object of chemical or, more correctly, physicochemical study, is the phase. In accordance with the definition given by Gibbs (1876), this term refers to homogeneous substances in equilibrium systems, separated by interfaces.

"The concept of a phase is more general than the modern chemical species which, as we have seen, refers only to substances of constant composition or definite compounds; the phase concept also covers the enormous class of homogeneous substances of variable composition, or solutions."*

Kurnakov then drew attention to the need for studying phases of variable composition, and to methods used for such investigations, based on measurement of physical properties of systems with variations in the component concentrations. The main characteristic of a compound of constant composition is the existence of a multiple or singular (special) points on "composition–property" diagrams.

Kurnakov wrote: "Thus we reach the conclusion that a definite compound is characterized not by the phase composition, as this is in general variable, but by the composition corresponding to the singular or Daltonian point on the phase-property diagrams."**

Kurnakov then gave a general definition of a chemical species, consistent with the laws of constant composition and multiple proportions: "a chemical species, corresponding to a definite chemical compound, is a phase which has singular or Daltonian points on its property curves. The composition corresponding to these points remains constant when the factors determining equilibrium in the system are varied."***

However, N. S. Kurnakov considered it necessary to extend the concept of a chemical species to compounds of variable composition (such as the γ-phase in the thallium–bismuth system), which cannot be characterized by singular points and, therefore, do not conform to the laws of constant composition and multiple proportions. Such compounds (or berthollides) are very common.

"The existence of species of variable composition," said Kurnakov at the conclusion of his paper, "widens the range of our ideas of chemical compounds."****

In developing these views, Kurnakov defined "establishment of a genetic relationship between existing phases and classification of species" as a task of chemical research. From this point of view, studies of phase diagrams became important in principle for formulation of the most fundamental concepts of physicochemical analysis and of chemistry in general – concepts of definite and indefinite chemical compounds. Kurnakov wrote: "Quantitative measurements of chemical composition – property diagrams reveal the existence of special types of phases, which provide the investigator with important criteria for determining the nature of a compound or chemical species."

The fruitful scientific and theoretical work of N. S. Kurnakov was summarized by him in two papers: "Singular points in chemical diagrams" (May 27, 1922, at the Third Mendeleev Congress), and "Continuity of chemical conversions of matter" (December 29, 1922, at the Annual Meeting of the Academy of Sciences). The

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* N. S. Kurnakov, Compounds and Chemical Species. Introduction to Physicochemical Analysis [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1940) 4th edition, pp. 10-11.

** N. S. Kurnakov, Introduction to Physicochemical Analysis [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1940) 4th edition, p. 16.

*** N. S. Kurnakov, Introduction to Physicochemical Analysis [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1940), 4th edition, p. 16.

**** N. S. Kurnakov, Introduction to Physicochemical Analysis [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1940), 4th edition, p. 16.

paper, "The compound and space," presented at the general assembly of the Fourth Mendeleev Congress on Chemistry in Moscow on September 20, 1925, belongs to the same series of theoretical generalizations.

Having demonstrated with many examples the value of "composition–property" diagrams, Kurnakov stated: "Without the graphical constructions of descriptive geometry, studies of chemical equilibrium systems, especially with large numbers of components, become impossible."**

The use of the geometrical method clearly shows that formation of substances of variable composition is a more general case of interaction of substances than the formation of definite compounds. Definite compounds are special cases, characterized by singular points on chemical diagrams.

"It should be noted," stated Kurnakov, "that solids of constant composition, used in chemical analysis, are regarded as the mainstay of the law of multiple proportions and of the atomistic theory. Therefore, variability of composition, as a general property of solid homogeneous substances, inevitably gave rise to concern about the accuracy and the fate of the fundamental law of chemistry, with all the consequences which would follow. Berthollet's continuity idea appeared incompatible with the concepts of Prout and Dalton. However, such fears are unfounded in reality. The existing results of physicochemical analysis now enable us to claim with complete confidence that both sides in this controversy are right, but that the Berthollet viewpoint is the more general.

"We must regard solutions and substances of variable composition or solvates as the main type of chemical conversion. Strange though it may seem at first sight, it is the continuity principle which must henceforth guard the inviolability of the law of constant composition, and must give precise geometrical characterization of the abrupt changes in formation of definite chemical compounds."***

Kurnakov's main interests were concentrated on studies of equilibrium systems, but he did not disregard studies of individual systems, and particularly their structure. He used the methods of crystal chemistry for this purpose.

The generalizations and fundamentally important conclusions cited above were subsequently confirmed in numerous investigations by Kurnakov himself and by his school.

Physicochemical analysis, which plays a very important part in various branches of the national economy, is continuing to develop rapidly. The classical methods of physicochemical analysis (conductivity, hardness, etc.), are being used in conjunction with crystal chemistry, solid-state physics, and new structural concepts in order to obtain deeper insight into the nature and forces of chemical bonding in definite compounds, studies of the structure of phases of variable composition, investigations of the nature of chemical interaction of components in various systems, and studies of phase equilibria and transitions. Physicochemical analysis is becoming increasingly interrelated with thermodynamics.

The future development of physicochemical analysis, which was created by our eminent chemist N. S. Kurnakov, is an important and highly promising task. Much importance attaches to searches for new quantitative relationships for variations of properties of systems with composition. It is also important to develop new methods for representing "composition–property" diagrams of multicomponent systems and to study their geometrical characteristics.

*N. S. Kurnakov, Introduction to Physicochemical Analysis [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1940), 4th edition, p. 31.

**N. S. Kurnakov, Introduction to Physicochemical Analysis [in Russian] (Izd. AN SSSR, Moscow-Leningrad, 1940), 4th edition, p. 34.

INTERATOMIC DISTANCES IN MOLECULES OF GASEOUS ALKALI METAL HALIDES

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Original article submitted April 21, 1959

One method of comparative calculation was used for calculating interatomic distances d in molecules of alkali halides; the calculated results are in good agreement with experimental data. This method was used for finding the approximate values of d_{Fr-X} (X = F, Cl, Br, I) and d_{Me-At} (Me = Li, Na, K, Rb, Cs).

Methods of comparative calculation can be widely used for determination of the values of various properties. In particular, this applies to the method based on comparison of the values of a given property in two series of similar substances. In the general case, this method corresponds to the approximate linear relationship

$$G_{II} = AG_I + B, \tag{1}$$

in which the properties G in series I and II of related compounds are compared (on a linear or a functional scale). The validity of this relationship has been demonstrated earlier by numerous examples (e.g., see [1,2,3]). In this paper, Eq. (1) is used in relation to the special case of interatomic distances d in gaseous molecules, i.e., it is used in the form

$$d_{II} = Ad_I + B, \tag{2}$$

which, with others, was considered in relation to a number of examples in [3].

Here we deal with calculation of d for gaseous alkali halides, i.e., we discuss the applicability of Eq. (2) in the form of the equation

$$d_{MeX} = A_X d_{MeBr} + B_X \tag{3}$$

and

$$d_{MeX} = A_{Me} d_{KX} + B_{Me}. \tag{4}$$

These are the only substances for which the experimental values of d are known very accurately (error of the order of 0.0001 A [4,5]). Equations (3) and (4) can be used most effectively for verifying the reliability of the comparative calculation method for determination of interatomic distances in gaseous compounds.

Several investigations [4, 6-8] have been concerned with calculations of d for these substances. The equation given in [4] gives an average deviation of 0.005 A from experimental values (for eight halides). In [6], the calculations were based on regular deviations from additivity in relation to the positions of the ions in the periodic system; the average deviation from the calculated results for five substances (LiCl, LiF, NaF, KF, RbF) was less than 0.015 A. The equation given in [7] gave an average deviation of 0.003 A for eight substances. This equation was used for calculating d for the same molecules as in [6]; the average difference between the results in [6] and [7] was 0.052 A. Finally, the relationship between d and certain physicochemical characteristics of the ions is considered in [8], and values of d_{FrX} are estimated.

TABLE 1

Coefficients of Eq. (3)

Molecule*	A_X	B_X
MeF	0,755	0,036
MeCl	0,9557	—0,0293
MeBr	(1,0000)	(0,0000)
MeF	1,0604	0,0575

*Me = Na, K, Rb, Cs, Fr.

TABLE 2

Coefficients of Eq. (4)

Molecule	A_{Me}	B_{Me}
LiX	0,9753	—0,5836
NaX	0,9200	—0,0931
KX	(1,0000)	(0,0000)
RbX	1,024	0,0562
CsX	1,0735	0,0436
FrX	1,075	0,113

*X = Cl, Br, I.

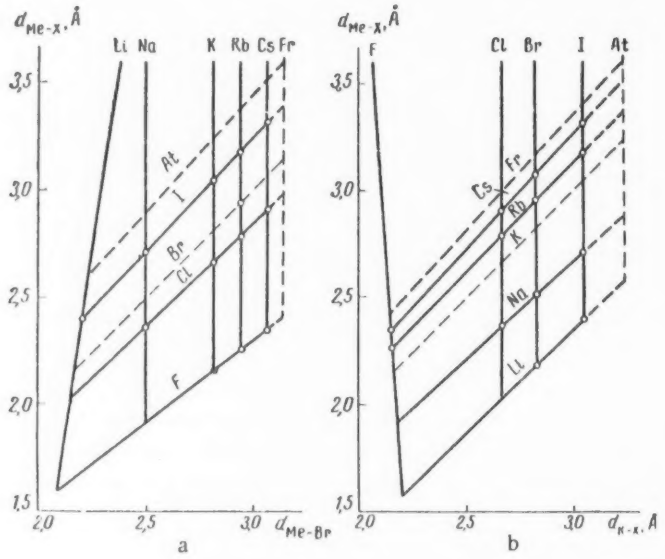

Fig. 1. Interatomic distances d (A) for gaseous alkali halides.

The most precise experimental data [4,5] were used for calculations by means of Eqs. (3) and (4). These experimental data were used for finding the coefficients in the equations. Their values are given in Tables 1 and 2, respectively. The results of calculations by Eqs. (3) and (4) are given in Table 3 and are plotted in Fig. 1.

If the coefficients of Eq. (3) for MeF are calculated from the available literature data on d_{CsF} [4] and d_{RbF} [5] (other fluorides were not studied), the results obtained (d_{LiF} = 1.735, d_{NaF} = 1.988, and d_{KF} = 2.188 A) are considerably higher than the values recommended in [7], which are probably the most reliable of the calculated data available at the present time; the discrepancy is especially large for LiF (about 0.25 A). If, on the other hand, the calculation is based on a value of d_{RbF} somewhat lower than is recommended in [4], and a value of d_{CsF} somewhat higher than that in [5], different values are obtained; these are given in the third column of Table 3 [the corresponding coefficients of Eq. (3) are given in Table 1]. It seems that the experimental values should lie between the two, closer to the latter for fluorides which have not been studied yet; this is also indicated by the results of calculations with the aid of Eq. (4).

According to Table 3, Eq. (3) agrees with experimental data (for 11 substances) with an average error of 0.0023 A, which diminishes to 0.0009 A if the experimental values of d_{RbF} and d_{CsF} are considered. The average error in calculations by Eq. (4) is only 0.0004 A, which is comparable with the precision of the experimental data. It must be noted that the calculation method used in [6] on the whole corresponded to Eq. (1). In fact,

TABLE 3

Values of Interatomic Distances d (A) in Molecules of Gaseous Alkali Halides

Molecule	d_{expt}*	d_{calc} by Equation	
		(3)	(5)
LiF	—	~1,61**	~1,60***
LiCl	—	~2,035**	2,0202
LiBr	2,1704		(2,1704)
LiI	2,3919	~2,395**	(2,3919)
NaF	—	1,925	~1,922***
NaCl	2,3606	2,3593	2,3602
NaBr	2,5020		2,5019
NaI	2,7115	2,7106	2,7119
KF	—	2,165	2,165***
KCl	2,6666	2,6668	
KBr	2,8207		
KI	3,0478	3,0475	
RbF	2,26554	2,259	2,265***
RbCl	2,7867	2,7883	2,7868
RbBr	2,9448		2,9445
RbI	3,1769	3,1773	3,1772
CsF	2,3453	2,355	2,347***
CsCl	2,9062	2,9058	2,9062
CrBr	3,0720		3,0715
CsI	3,3150	3,3157	3,3154
FrF	—	2,414	2,411***
FrCl	—	2,976	2,980
FrBr	—		3,145
FrI	—	3,392	3,390
Average deviation		0,0023	0,0004

*From data of [4]; for RbF, from [5].

**Found from the $d_{MeX}-d_{MeBr}$ graph (Fig. 1a).

***Found from the $d_{MeX}-d_{KX}$ graph (Fig. 1b).

if the latter is written, for the special case of Eq. (4), as

$$\frac{d_{MeI}-d_{MeBr}}{d_{MeBr}-d_{MeCl}}=A_{Me}, \qquad (5)$$

the correspondence is obvious.

The regular variation of A_{Me} with the position of Me in the periodic system, noted in [6] (see Fig. 1), applies not only to the property in question, but is a general relationship. This is demonstrated directly from the diagrams given for various properties in [1,2,3].* Certain assumptions were made in [6], and these led to some discrepancies between the values of d for a number of molecules and the values found in the present investigation. First, it was assumed that $A_{Li}=A_{Na}$, and then that $A_{Na}/A_{Li}=A_{Na}/A_K$; as Table 2 shows, this assumption is not very exact. Second, in [6], it was assumed that the following expression is valid:

$$\frac{d_{MeCl}-d_{MeF}}{d_{MeI}-d_{MeBr}}=A_{Me}. \qquad (6)$$

Apparently this assumption is not very accurate either; the MeF line in Fig. 1b is not vertical. It is true that, as was noted earlier, the results of the present calculation are probably not as reliable for MeF as for the other halides. Direct confirmation of the above conclusion is therefore difficult. However, two indirect considerations may be noted. First, while the values of d calculated from (3) and found in [6] differ significantly (Δ_{av} = 0.022 A), the differences between the former and those recommended in [7] are not large (Δ_{av} = = 0.009 A). At the same time, Krasnov regards the values of d_{MeF} found in [7] as more reliable than those calculated in [6], assuming that the experimental values would be closer to the former. Moreover, the sign of the deviations of d given in [6] from those in [7] is the same for all substances which have not been studied; this may be regarded as evidence that the values of d recommended in [6] are somewhat too low. Moreover, analogous deviations for compounds of the second group of the periodic system for other properties, in particular for ionization potentials [2], and also, but to a lesser extent, for interatomic distances in alkaline-earth halide molecules [3].

The values of d for molecules formed by electronic analogs (elements of the principal subgroup of group I on the one hand, and elements of the principal subgroup of group VII on the other) constitute a system of quantities. Therefore, the results obtained (in particular, Fig. 1), can be used for estimating d_{FrX} and d_{MeAt}. Reliable extrapolation is difficult, owing to lack of precise data on the Fr ion [9,10]. For calculation of D_{FrX} we can use the approximate linear expression

$$d_{Me_{II}X}=Ad_{Me_{I}X}+B, \qquad (7)$$

in which the interatomic distances in alkaline-earth and alkali-metal halides are compared. Figure 2 shows that the results calculated from Eq. (7) lie within the error limits of the values of $d_{Me_{II}X}$ [11].** From the

*For example, see the graphs representing comparative calculations of ionization potentials, lattice energies, heats of formation, and other properties in [1] and [2], and Figs. 10, 11, 14, and 15 in [3].

**These are marked by vertical intercepts in the diagram. The lines for fluorides and iodides only are drawn, so that the figure should not be too cumbersome, and the positions of the points are indicated on the first of the lines only.

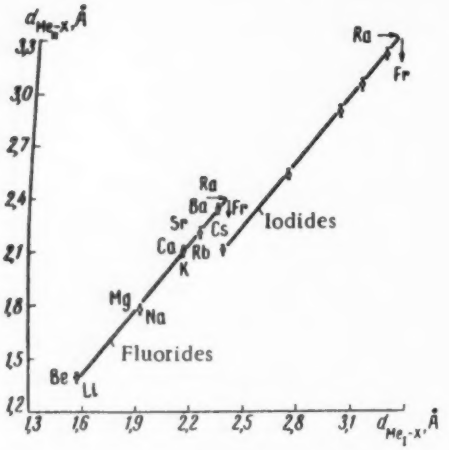

Fig. 2. Relationship between the interatomic distances d (A) in gaseous halides of alkali and alkaline-earth metals.

values of d_{RaX} [3] we find d_{FrX}:d_{FrF} = 2.41; d_{FrCl} = 2.98; d_{FrBr} = 3.15; d_{FrI} = 3.39 A (dash line in Fig. 1). The values are smoothed with the aid of Eq. (4); the coefficients of the latter are given in Table 2, and the calculated results in Table 3. The latter also includes values of d_{FrX} calculated from Eq. (3). The values found in this way are approximate [they are influenced by the imprecision of $d_{Me_{II}X}$, the approximate character of (7), and by the errors in the values used for d_{RaX}]. However, first, they are close to those found in [8] (Δ_{av} = 0.016 A), and second, we wished to use an approximate relationship of the form of (1) which, as far as we know, has not been used previously.

Analogous calculations of D_{MeAt} can, as yet, give only tentative results. Such calculations were performed with the use of the approximate value of the crystal radius of the ion $r_{At'}$ = 2.34, given in [12]. The results are shown in Fig. 1.

SUMMARY

One of the possible methods of comparative calculation was used for calculating interatomic distances d in gaseous alkali halides. The average deviation of the calculated values of d from experimental values was 0.0012 A (for 15 substances).

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THERMOCHEMICAL METHOD FOR DETERMINATION OF THE COORDINATION NUMBERS OF IONS IN AQUEOUS SOLUTIONS

(Dedicated to the Memory of Anatolii Fedorovich Kapustinskii)

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The relationship between the differential heats of solution of HCl and the coordination numbers of ions in solution is considered. The heats of solution of K_2SO_4 in aqueous HCl solutions at 25° were measured in a calorimeter with an isothermal jacket. Correlation of the experimental results with the dependence of the differential heats of solution of HCl on concentration confirms the expression forming the basis of the thermochemical method for determination of the coordination numbers of ions in aqueous solutions.

The thermochemical method for determination of the coordination numbers of ions in aqueous solutions is based on measurements of the heats of solution of salts in water and in aqueous acid solutions of various concentrations [1]. The dependence of the heat of solution (L) of the salt at a constant and low final concentration in solution on the acid concentration (m) is determined. Here L is expressed in kilocalories per mole of dissolved salt, and m in moles of acid per 50 moles of water (most of the work has been with HCl). Calculations of the coordination numbers of ions in dilute solutions are based on the following behavior of the hydrogen ion. Protons present in acid solutions in excess over the composition of the H_2O molecule are not attached to definite water molecules to form H_3O^+ ions, but move continuously from one water molecule to another; they confer to the water molecules a certain small average positive charge ϵ, which increases with the acid concentration.*

In accordance with the accepted model, we can assume that

$$\varepsilon = km, \tag{1}$$

where k is a proportionality factor which may approximately be assumed independent of the acid concentration [1]. The value of k can be estimated. Thus, when m = 1, i.e., when one mole of acid (for example, HCl) is present in solution with 50 moles of water, one proton is distributed between 50 water molecules, so that a charge e/50 (e = the electronic charge) can be ascribed to each water molecule. However, the effective charge $\epsilon < e/50$, because we must take into account the degree of dissociation of the acid and shielding of the charge ϵ by the electron cloud of the water molecule. Therefore, we can write

$$k = \gamma \frac{e}{50}, \tag{2}$$

* The model used for consideration of the state of hydrogen ions in aqueous solutions was formerly characterized as a certain "proton gas" [1,2], distributed over the poles of the water molecules.

where $\gamma < 1$. It is assumed in calculations of the coordination numbers of ions in solutions that the ions are immediately surrounded by water molecules only. This assumption is undoubtedly valid for dilute solutions. It was shown [1] (and this is very significant) that, in accordance with this assumption, only the charges of the water molecules closest to the selected ion need be taken into account in calculating the energy of interaction of ions with excess protons ("proton gas"). However, this simplification cannot be used at very low HCl concentrations.

With these assumptions, it was possible to derive [1] the following expression for $\beta = -\Delta L/\Delta m$ (with the thermodynamic sign convention $\beta = \Delta L/\Delta m$):

$$\beta = K\left(\frac{n_c}{R_c} - \frac{n_a}{R_a}\right), \tag{3}$$

where K = 2.4 Nek (N is the Avogadro number, and the factor 2.4 represents conversion from ergs to kilocalories, and angstroms to centimeters); this is a coefficient determined from experimental data; n_c and R_c are the coordination number and radius (in A) of the first coordination sphere of the cation in solution, and n_a and R_a are the corresponding values for the anion. In accordance with Eq. (3), the dependence of L on m is determined by the contributions of the different ions to β,

$$K\frac{n_i}{R_i},$$

or their contributions to the heat of solution L,

$$K\frac{n_i}{R_i}m.$$

This communication is concerned with refinement of the theory of the thermochemical method for determination of coordination numbers of ions in aqueous solutions, and with an additional experimental verification of Eq. (3).

The thermochemical method involves the use of the relationship between the heats of solution of HCl in its aqueous solutions and the acid concentration in the solvent. Let small and always equal numbers of moles of HCl (Δs) be added to a solvent which is a relatively dilute aqueous solution of HCl containing s moles of HCl and M_l moles of H_2O [the concentration of such a solution is $m = (50/M_l)s$]; the effect of m on the heat of solution is then determined. The values of $\Delta H/\Delta s$, where H is the enthalpy of the system, are measured. At low values of Δs the measured value almost coincides with the derivative $(\partial H/\partial s)_{p,T,M_l}$ (the differential heat of solution of HCl). If the determinations are performed under atmospheric pressure, the term pv may be disregarded and it may be assumed that the quantity $\partial E/\partial s$, where E is the internal energy of the system, varies. We shall now consider the relationship between $\partial E/\partial s$ and m.

It can be assumed that the part of E dependent on m (at least in relatively dilute HCl solutions where, as was noted above, we need take into account the interaction of the ions only with the charges ϵ of the nearest water molecules) is the electrostatic energy of interaction of the charges ϵ with Cl^- anions, and with each other. Let us first derive the contribution, dependent on m, of the Cl^- ions to E. In accordance with (1), $\epsilon = km$, the number of g-ions of Cl^- in solution is $(M_l/50)m$, and their energy of interaction with the charges ϵ of the nearest water molecules (in kilocalories per g-ion), is

$$E^m_{Cl^-} = -2{,}4N\frac{n_{Cl^-}}{R_{Cl^-}}kme\frac{M_l}{50}m = -K\frac{n_{Cl^-}}{R_{Cl^-}}m^2\frac{M_l}{50}$$

($E^m_{Cl^-}$ corresponds to attraction; the thermodynamic sign convention is used).

$$\frac{\partial E^m_{Cl^-}}{\partial s} = \frac{\partial E^m_{Cl^-}}{\partial m}\frac{dm}{ds}, \tag{4}$$

and since

$$\frac{dm}{ds} = \frac{50}{M_l}, \tag{5}$$

therefore,

$$\frac{\partial E^m_{Cl^-}}{\partial s} = -2K \frac{n_{Cl^-}}{R_{Cl^-}} m. \quad (6)$$

This last value represents the contribution of the Cl^- ions to the differential heat of solution of HCl.

We now write the contribution, dependent on m, of the H^+ ions to E (this term corresponds to repulsion, and is therefore positive by our sign convention):

$$E^m_{H^+} = 2{,}4N \frac{n_{H^+}}{R_{H^+}} k^2 m^2 M_l,$$

since the number of particles with charge ϵ in solution (the number of $H_{2+\frac{\epsilon}{e}} O^{\frac{\epsilon}{e}+}$ ions [1]) is evidently equal to the number of water molecules (NM_l). The values of n_{H^+} and R_{H^+} can probably be taken as approximately equal to the corresponding values for water molecules in water. From (4) and (5) we have

$$\frac{\partial E^m_{H^+}}{\partial s} = 4{,}8N \frac{n_{H^+}}{R_{H^+}} k^2 50m;$$

but, in accordance with (2), $k \cdot 50 = \gamma e$ and, therefore,

$$\frac{\partial E^m_{H^+}}{\partial s} = 4{,}8\gamma N \frac{n_{H^+}}{R_{H^+}} kem = 2\gamma K \frac{n_{H^+}}{R_{H^+}} m. \quad (7)$$

Thus, Cl^- and H^+ ions make contributions corresponding to (6) and (7), respectively, to the differential heat of solution of HCl (L_{HCl}), i.e.,

$$L_{Cl^-} = 2\gamma K \frac{n_{H^+}}{R_{H^+}} m - 2K \frac{n_{Cl^-}}{R_{Cl^-}} m$$

and an expression of the type of (3) can be written for the relationship between L_{HCl} and m:

$$\beta_{HCl} = \frac{\Delta L_{HCl}}{\Delta m} = K\left(2\gamma \frac{n_{H^+}}{R_{H^+}} - 2\frac{n_{Cl^-}}{R_{Cl^-}}\right). \quad (8)$$

Analogously, it is to be expected that, in the range of HCl concentrations in which the assumptions used in derivation of Eq. (8) are valid, L_{HCl} should be approximately (as the expression derived is approximate), a linear function of m.

It should be noted that the factors 2 appear because both the magnitude of the charge ϵ and the number of g-ions of Cl^- in solution increase. When salts are dissolved in aqueous acid solutions, only the number of ions in solution changes, and the factors 2 are therefore absent.

Evidently, for comparison of Eq. (8) with experimental data, we can use the well-known dependence of the partial molar enthalpy of HCl ($\bar{L}_2$) in aqueous solution on concentration. In fact, $(\partial H/\partial s)_{p,T,M_l} = \bar{L}_2 + \bar{L}^\circ_2$, where $\bar{L}^\circ_2$ is a constant associated with the choice of the standard state, and which is independent of the HCl concentration. Therefore, the dependence of $(\partial H/\partial s)_{p,T,M_l} = L_{HCl}$ on m coincides with the dependence of $\bar{L}_2$ on m.

In Fig. 1, the relationship between $\bar{L}_2$ and m is plotted in accordance with literature data [3]. It is known [3] that values of $\bar{L}_2$ determined calorimetrically are in good agreement with values calculated from emf data. Figure 1 shows that the relationship between $\bar{L}_2$ and m is approximately linear at $m > 0{,}09$, in agreement with Eq. (8). At $m < 0{,}09$ it is evidently insufficient to take into account interaction of the ions with the charges of only the nearest water molecules; at such concentrations it can no longer be assumed that the action of the charges ϵ beyond the limits of the first coordination sphere is compensated by the action of the Cl^- ions ([1], pp. 123, 124). For the concentration range $m > 0{,}09$, the value $\beta_{HCl} = \Delta L_{HCl}/\Delta m = \Delta\bar{L}_2/\Delta m = 509$ cal (mole[m])$^{-1}$ was calculated by the method of least squares.

Variations of the heats of solution of K_2SO_4 in aqueous HCl solutions with m were of interest in connection with the experimental verification of the thermochemical method for determination of the coordination numbers of ions in solutions. These heats were measured at 25° in a calorimeter with an isothermal jacket. The

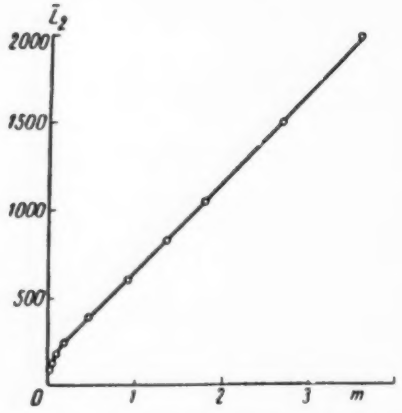

Fig. 1. Variation of the partial molar enthalpies of HCl in aqueous solutions ($\bar{L}_2$) with concentration (m) at 25°.

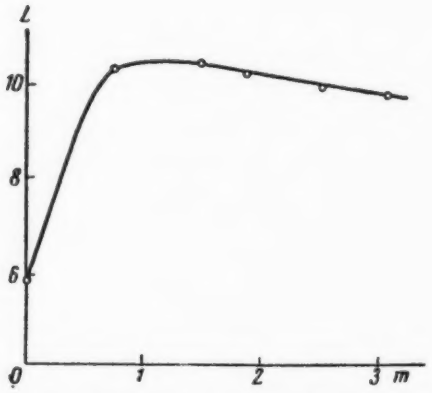

Fig. 2. Variation of the heat of solution of K_2SO_4 in aqueous HCl solutions (L) with the HCl concentration (m) at 25°.

Heats of Solution of K_2SO_4 in Aqueous HCl Solutions at 25°•

m	0,00	0,73	1,48	1,86	2,50	3,06
L	5,81	10,32	10,50	10,25	10,03	9,84

• The thermodynamic sign convention is used.

experimental procedure was as described previously [4]. The amounts of K_2SO_4 (c.p., recrystallized) taken were such that the final concentration of the salt in solution was approximately 0.05 mole of K_2SO_4 to 50 moles of water. The values found for the heats of solution (L) are given in the table. Here L is given in kilocalories per mole of K_2SO_4 dissolved.

The L–m relationship is plotted in Fig. 2. As in other sulfate solutions, the region of the L–m curve at $m < 1$ is associated with a shift of the equilibrium $SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$ [1]. For determination of $\beta_{K_2SO_4} = \Delta L/\Delta m$, we used the region of the L–m curve at $m > 1$, where this relationship was close to linear. It was found that at 25°, $\beta_{K_2SO_4} = 402$ cal/(mole[m]).

The validity of Eq. (3) can be verified with the aid of the experimental relationships between m and the heats of solution of K_2SO_4, $KHSO_4$, KCl in aqueous HCl solutions, and of the differential heats of solution of HCl. When s moles of K_2SO_4 is dissolved in aqueous HCl solution at $m > 1$, the following processes take place:

1. 2s g-ions of K^+ goes into solution;

2. s g-ions of H^+ leaves the solution, as this quantity combines with s g-ions of SO_4^{2-}: $SO_4^{2-} + H^+ \rightarrow HSO_4^-$;

3. s g-ions of HSO_4^- appears in solution. By reasoning similar to that used in calculating the contributions of Cl^- and H^+ ions to β_{HCl}, it can be easily shown that the variation of $L_{K_2SO_4}$ with m (the value of $\beta_{K_2SO_4}$) is determined by the ionic contributions $2K(n_{K^+}/R_{K^+})$, $-2\gamma K(n_{H^+}/R_{H^+})$, $K(n_{Cl^-}/R_{Cl^-})$, and $K(n_{HSO_4^-}/R_{HSO_4^-})$. The contributions corresponding to H^+ and Cl^- ions should be explained. Formation of HSO_4^- anions leads to removal of Δs g-ions of H^+, i.e., to the reverse of the process which was considered in calculation of β_{HCl}. Therefore, the contribution of the H^+ ion differs from that calculated for β_{HCl} in sign only, and has the value $-2\gamma K(n_{H^+}/R_{H^+})$. The number of Cl^- ions in the solution does not change during the dissolution process, and only the charge ϵ decreases from km to $k[m - (50/M_l)\Delta s]$. This gives rise to the contribution $+K(n_{Cl^-}/R_{Cl^-})$. We have

$$E^m_{Cl^-} = -2{,}4N\frac{n_{Cl^-}}{R_{Cl^-}}\varepsilon e\frac{M_l}{50}m_{Cl^-}$$

(evidently before dissolution of K_2SO_4, $m_{Cl^-} = m_{H^+} = m$). We look for a value of $\Delta E^m_{Cl^-}/\Delta s$ close to $\partial E^m_{Cl^-}/\partial s$ at low Δs.

However,

$$\frac{\partial E^m_{Cl^-}}{\partial s} = \frac{\partial E^m_{Cl^-}}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial s}.$$

$$\varepsilon = km_{H^+},\ d\varepsilon = kdm_{H^+} = -k\frac{50}{M_l}ds,\quad \frac{\partial \varepsilon}{\partial s} = -k\frac{50}{M_l}$$

$$\frac{\partial E^m_{Cl^-}}{\partial s} = 2{,}4N\frac{n_{Cl^-}}{R_{Cl^-}}kem_{Cl^-} = K\frac{n_{Cl^-}}{R_{Cl^-}}m_{Cl^-}, \text{and } m_{Cl^-} = m.$$

Therefore,

$$\beta_{K,SO_4} = K\left(2\frac{n_{K^+}}{R_{K^+}} - 2\gamma\frac{n_{H^+}}{R_{H^+}} + \frac{n_{Cl^-}}{R_{Cl^-}} - \frac{n_{HSO_4^-}}{R_{HSO_4^-}}\right). \tag{9}$$

But Eq. (8) was derived for β_{HCl}, and

$$\beta_{KHSO_4} = K\left(\frac{n_{K^+}}{R_{K^+}} - \frac{n_{HSO_4^-}}{R_{HSO_4^-}}\right) \tag{10}$$

and

$$\beta_{KCl} = K\left(\frac{n_{K^+}}{R_{K^+}} - \frac{n_{Cl^-}}{R_{Cl^-}}\right). \tag{11}$$

Comparing (9) with (8), (10), and (11) we see that

$$\beta_{K,SO_4} = \beta_{KHSO_4} - \beta_{HCl} + \beta_{KCl}.$$

At 25°, $\beta_{KHSO_4} = 96$ [5], $\beta_{KCl} = 11$ [1], and $\beta_{HCl} = 509$ cal/(mole[m]). Therefore,

$$\beta_{KHSO_4} - \beta_{HCl} + \beta_{KCl} = -402 \text{ cal/(mole[}m\text{])}.$$

At the same time, it was found, in the present investigation, that at 25° $\beta_{K_2SO_4} = -402$ cal/(mole[m]). This exact agreement is certainly accidental. However, there is no doubt that the experimental results confirm the validity of Eq. (3), which forms the basis of the thermochemical method for determination of the coordination numbers of ions in aqueous solutions.

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SYSTEM OF ELECTRONEGATIVITIES FOR AQUEOUS SOLUTIONS

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The electronegativity concept is extended to aqueous solutions. Electronegativities of atoms are calculated by Mulliken's method; when hydration is taken into account, the values for metals are sharply decreased, while nonmetals retain the standard values. As a result, the electronegativity difference increases and the bonds approach the ionic type.

The concept of "electronegativity" as the affinity of an atom in a molecule to valence electrons is expressed quantitatively by various electronegativity systems based on measurements of the physical characteristics of homopolar molecules. Tables of electronegativities derived by various methods agree satisfactorily with each other, and, therefore, the states of atoms in molecules can be reliably characterized by the average values [1]. At the same time, it was shown [1] that electronegativities of atoms in the isolated state, i.e., of free radicals, are approximately 25% greater than in the corresponding molecules: $x_A > x_{A_2}$. This naturally raised the question of whether the electronegativity of an atom in general depends on its nearest neighbors.

The case of greatest practical importance in chemistry is that of aqueous solutions. The present paper therefore represents a first attempt to formulate a system of "aqueous" electronegativities of atoms. Another reason why this problem should be solved is that the electronegativity concept, used successfully in the most diverse branches of physical chemistry, is not used as yet to any extent in the theory of solutions, as it cannot account even for the electrolytic dissociation of salts. Indeed, the electronegativity difference $X_{Hal} - X_{Me}$, even for alkali chlorides and fluorides, is such that the amount of ionic character in accordance with Pauling's curve [2] cannot be more than 80%, while in the case of bromides and iodides the amount of ionic character is only 40-50%. In the case of alkaline-earth halides, and even more so in the case of elements of the zinc subgroup, the amount of ionic character in the bond is still less, and often does not exceed 20-30%, although it is known that these salts (apart from mercury halides) are highly dissociated in solution. This contradiction between the requirements of the electronegativity theory and experimental chemical data needs to be resolved.

We determined the electronegativities of atoms in aqueous solutions by Mulliken's method [3,4], i.e., from the ionization potentials I and electron affinities E. Our calculation method involves calculation of the expression

$$E_s + I_s/E_v + I_v,$$

where the subscripts s and v refer to the states of the atom in solution and in vacuo, respectively, with subsequent introduction of the appropriate correction into the standard value for the electronegativity of the given element.

The electron exit work function in aqueous solution, i.e., the ionization potential in aqueous solution I_s (ΣI_s for multivalent ions), can be calculated from known values of I_v (or ΣI_v, respectively), and hydration energies ΔZ_h. It was shown by Mikhailov and Drakin [5] that the equation for this calculation is of the form

$$\Sigma I_s = \Sigma I_v + \Delta Z_h - A_c + RT \ln (1/24{,}4), \qquad (1)$$

where A_c is the work of formation of the cavity occupied by the ion. They also proposed an approximate theoretical method for calculation of I_s, which does not require a knowledge of the energy of hydration. The values of I_s, calculated by the method described earlier [5], are denoted by $I_s^{calc.}$.

Analogously, electron affinities E_s in aqueous solution can be found from the expression

$$E_s^g = E_v - \Delta Z_h + A_c - RT \ln (1/24{,}4). \quad (2)$$

Values of ΣI_s for cations with inert gas electron configurations, calculated from these equations, are given in Table 1, and values of Σ_s for anions, in Table 2. Values of ΣI_v were taken from Table [6], values of ΔZ_h from [5] and partly from [7]; values of E_v for halogens were taken from [8], and for S^{2-} from [9]. Values of A_c were calculated as described in [10].

It is interesting to note that the ratio $\Sigma I_s / \Sigma I_v = k_1$ is fairly constant, with an average value of 7 ± 2%. The constancy is even better for elements of the same period: 11% Na, 14% Mg, 12% Al, and average 12%; 7% K, 8.3% Ca, 11% Sc, and average 9%; 5% Rb, 7.8% Sr, 6.1% Y, and average 6%; 3% Cs, 7.2% Ba, 5.8% La, and average 5%. For halogens, the ratio E_s / E_v is also constant, and has the value 210 ± 10%.

Table 3 contains values of ΣI_s for cations which do not have inert gas electron configurations. Here the ratio $\Sigma I_s / \Sigma I_v$ is again fairly constant, with an average value of 21 ± 5%. The values by periods are: for Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, average 17.6%; for Ag, Cd, In, Sn, average 25.0%; for Hg, Tl, Pb, average 29.3%. It can be seen that values of ΣI_s for ions not of inert gas configuration are regularly greater than for ions of the inert gas type with the same charge Z and radius $\underline{r}$. The explanation is that the excess field of force of an ion not of the inert gas type, numerically characterized by the corresponding ionization potential difference, is only partially saturated as the result of hydration. Drakin and Mikhailov [10] previously assumed, in calculation of the hydration energies of ions not of the inert gas type, that the degree of saturation of this excess field of force is approximately 0.5. In the reverse problem, calculation of ΣI_s from experimental data on hydration energies, this coefficient can be determined more precisely. The data needed for the calculation are contained in Table 3. Here $\Sigma I_v'$ represents the total ionization potential for a cation of the inert gas type with the same values of Z and $\underline{r}$, found by linear interpolation in $\Sigma I_v - r_{aq}$ coordinates [10]. Here $\Delta\Sigma I_v$ and $\Delta\Sigma I_s$, respectively, are the differences $\Sigma I_v - \Sigma I_v'$ and $\Sigma I_s - \Sigma I_s^{calc}$. It follows from these data that the values of ΣI_s found from Eq. (1) for uni- and bivalent ions exceed the calculated values on the average by 64 ± 16% of the excess ionization energy. Therefore, on the average, 36 ± 16% of the excess field of force of an ion not of the inert gas type is saturated as the result of hydration.

From the foregoing, it is possible to estimate ionization energies in solution for positively charged halogen ions also. The following formula was used for the calculations:

$$I_s = I_s^{calc} + 0{,}64\,(I_v^g - I_v^g). \quad (3)$$

The crystal radii r_{cr} of positively charged ions were calculated from Sanderson's formula [11]. The calculation results are summarized in Table 4.

The above values were used in the electronegativity calculations. The electron affinities of metal atoms were disregarded, because these values are small [12], and often not known to a sufficient degree of accuracy. Therefore, in the case of metals, the values of k_1 given in Tables 1 and 3 were merely used as correction factors. The ratio $k_0 = E_s + \Sigma I_s / E_v + \Sigma I_v$ was used for halogens and sulfur; not the standard values of their electronegativities, but values increased by 25%, were used as the initial data, because I_v and E_v directly characterize free atoms but not atoms contained in molecules (see [1]).

Table 5 contains electronegativity values in aqueous solutions calculated as described above; the calculations were based on values of $\underline{x}$ given in Batsanov's recent survey [1]. The values in Table 5 are correct to the first decimal place, while the hundredths of relative electronegativity units are merely approximate.

A number of interesting conclusions may be drawn from this table. First, the electronegativities of electropositive elements in aqueous solutions are considerably lower than the standard values, whereas the values for halogens change very little. Second, the differences between electronegativities of metals are sharply diminished; whereas, under standard conditions, Δx is often 1.0 and over, in the "aqueous" system the maximum value of Δx does not exceed 0.5; this is also in good agreement with the well-known equalization of salt properties in aqueous

TABLE 1

Values of I_s for Cations of the Inert Gas Type

Ion	ΣI_v, ev	$-\Delta Z_h$, ev	A_c, ev	ΣI_s, ev	$k_1 = \Sigma I_s/\Sigma I_v$, %	Ion	ΣI_v, ev	$-\Delta Z_h$, ev	A_c, ev	ΣI_s, ev	$k_1 = \Sigma I_s/\Sigma I_v$, %
Li^+	5,37	5,1	0,27	−0,1	0	Sr^{2+}	16,54	14,6	0,56	1,3	7,8
Na^+	5,09	4,1	0,38	0,6	12	Ba^{2+}	15,17	13,3	0,71	1,1	7,2
K^+	4,32	3,3	0,62	0,3	7	Ra^{2+}	15,40	13,0	0,78	1,5	9,7
Rb^+	4,19	3,1	0,76	0,2	5	Al^{3+}	53,14	46,8	0,18	6,1	12
Cs^+	3,86	2,8	0,90	0,1	3	Sc^{3+}	45,69	40,4	0,30	4,9	11
Be^{2+}	27,42	24,8	0,11	2,4	8,8	Y^{3+}	39,4	36,5	0,42	2,4	6,1
Mg^{2+}	22,73	19,3	0,29	3,1	14	La^{3+}	36,1	33,4	0,53	2,1	5,8
Ca^{2+}	18,12	16,1	0,42	1,5	8,3						

TABLE 2

Electron Affinities in Aqueous Solution

Ion	E_v, ev	$-\Delta Z_h$, ev	A_c, ev	E_s, ev	$k_2 = E_s/E_v$, %	Ion	E_v, ev	$-\Delta Z_h$, ev	A_c, ev	E_s, ev	$k_2 = E_s/E_v$, %
F^-	3,56	4,5	0,26	8,4	240	I^-	3,17	2,7	0,90	6,8	210
Cl^-	3,75	3,4	0,56	7,8	210	S^{2-}*	−4,10	13,6	0,52	10,1	—
Br^-	3,51	3,1	0,68	7,4	210						

*E_v and E_s represent affinities for two electrons.

TABLE 3

Values of I_s for Cations not of the Inert Gas Type

Ions	ΣI_v, ev	$-\Delta Z_h$, ev	A_c, ev	ΣI_s, ev	$k_s = \Sigma I_s/\Sigma I_v$, ev	$\Sigma I'_v$, ev	ΣI_v, ev	$\Sigma I_s^{calc.}$, ev	ΣI_s, ev	$\Delta\Sigma I_s/\Delta\Sigma I_v$, %
H^+	13,54	11,5	0	2,0	15	—	—	—	—	—
Cu^+	7,67	5,8	0,37	1,4	18	5,12	2,55	0,39	1,0	39
Ag^+	7,58	4,8	0,48	2,2	29	4,76	2,82	0,22	2,0	71
Tl^+	6,08	3,3	0,76	1,9	31	4,19	1,89	0,07	1,8	95
Zn^{2+}	27,41	20,4	0,30	6,6	24	21,89	5,52	2,82	3,8	69
Cd^{2+}	25,74	18,3	0,42	6,9	27	18,61	7,13	1,86	5,0	70
Hg^{2+}	28,96	19,3	0,48	9,1	31	17,67	11,29	1,56	7,5	66
Fe^{2+}	23,73	19,4	0,30	4,0	17	21,89	1,84	2,86	1,1	60
Co^{2+}	25,27	20,8	0,29	4,1	16	22,07	3,20	2,90	1,2	38
Ni^{2+}	26,48	21,2	0,29	4,9	18	22,73	3,75	3,12	1,8	48
Cu^{2+}	28,00	21,0	0,29	6,6	24	22,57	5,43	3,12	3,5	64
Sn^{2+}	22,10	15,9	0,42	5,7	26	18,45	3,65	1,82	3,9	107
Pb^{2+}	22,28	15,8	0,62	5,8	26	16,11	6,17	1,04	4,7	76
Mn^{2+}	21,91	18,8	0,34	2,7	12	20,59	1,32	2,34	0,4	30
Ga^{3+}	57,02	47,5	0,20	9,2	16	51,74	5,28	10,15	−0,9	−17
In^{3+}	52,37	42,2	0,35	9,7	18	43,29	9,08	5,81	3,9	43
Tl^{3+}	56,00	42,7	0,43	12,8	23	39,68	16,32	4,81	8,0	49
Ti^{3+}	48,80	42,4	0,23	6,1	12	49,76	−0,96	9,5	−3,4	—
Fe^{3+}	55,42	44,4	0,22	10,7	19	50,33	5,09	9,80	0,9	1

TABLE 4

Values of I_s for Halogens and Sulfur

Ion	r_{cr}, A	I_s^{calc}, ev	I_v, ev	I'_v, ev	I_s, ev	$k_0=E_s+\Sigma I_s/E_v+\Sigma I_v$, %
F^+	0,57	1,33	17,46	5,66	8,9	82
Cl^+	0,77	0,78	13,01	5,37	5,7	80
Br^+	0,91	0,52	11,82	5,19	4,8	79
I^+	1,04	0,35	10,43	4,96	3,8	79
S^{2+}	0,67	4,43	33,67	23,90	10,7	70

solutions. Finally, hydrogen is displaced considerably in the electronegativity scale, so that hydrogen in aqueous solutions has features of similarity with metals (compare with [13]).

Thus, the main conclusion drawn from the proposed system of electronegativities is in good agreement with the sharp increase in the ionic character of the bonds in inorganic compounds, i.e., with the phenomenon of electrolytic dissociation, and it reflects the role of ion hydration in this process. Table 6 contains average values of bond polarities in halides of groups I and II of the periodic system, in the molecular state and in aqueous solutions. Table 6 shows that the ionic character of the bonds in halides of any metals in aqueous solutions exceeds 50%; correction for the coordination number [14], which varies from 4 to 6 in solutions, would make the bond polarities even greater. This result eliminates the contradiction between the electronegativity concept and the existence of electrolytic dissociation of inorganic compounds in aqueous solutions which, of course, can occur only in predominantly ionic substances.

The values given for the degree of ionic character of the bonds also accounts for the difference between reactions of oxidation of compounds containing cations not of the inert gas configuration in the solid state and in aqueous solutions. Let us consider, in illustration, the oxidation of MnS. The action of chlorine on crystalline manganese sulfide gives $MnSCl_2$ [15], whereas, in aqueous solution, the same oxidizing agent displaces sulfur with formation of $MnCl_2$. This difference is explained as follows. The polarity of the Mn–S bond ($x_{Mn^{II}} = 1.4$ and $x_S = 2.6$) in the molecular state is 26%, whereas in aqueous solution ($x_{Mn} = 0.18$ and $x_S = 2.28$) it is 55%. Therefore, the manganese receives 0.74e from each bond in the first case, and 0.45e in the second. In a crystal the manganese atom receives 0.74e × 4 = 2.96e from all the sulfur atoms surrounding it in the tetrahedron, while in presence of water in formation of a hydrated MnS molecule it receives only 0.90e (if Mn is tetrahedrally surrounded by sulfur atoms in aqueous solution the charge from the bonds is 0.45e × 4 = 1.80e). Since we are considering bivalent manganese, the effective charge on the manganese atom in the crystalline sulfide is −2.96e + + 2e = −0.96e, and in presence of water it is −0.90e + 2e = +1.1e (or −1.80e + 2e = +0.20e). It follows unequivocally from this calculation that the action of an oxidizing agent on crystalline MnS must increase the valence of the metal, and in aqueous solution sulfur should be oxidized; this is found to be so in practice.

The "aqueous" system of electronegativities can also be used for solving problems in connection with stabilities of complex compounds, hydrolysis processes, extraction with organic solvents, catalytic action of water, etc., but detailed consideration of these problems is beyond the scope of our present work.

Compilation of experimental data on solvation energies in nonaqueous solutions would evidently make it possible to formulate the corresponding electronegativity systems; this would permit deeper investigations into physicochemical processes in these media.

SUMMARY

1. The electronegativities of 36 elements in aqueous solutions have been calculated.

2. The electronegativities of metals in aqueous solutions are considerably lower than the standard values. However, electronegativities of nonmetals remain almost unchanged, and bonds therefore become more ionic in aqueous solutions.

3. The proposed electronegativity system accounts for some peculiarities in chemical reactions in aqueous solutions.

TABLE 5

System of Electronegativities for Aqueous Solutions

Periods \ Groups	1a	2a	3a	4a	7a	8a	1b	2b	3b	4b	6b	7b
I	H 0,32											
II	Li 0	Be 0,13										F 4,01
III	Na 0,11	Mg 0,17							Al 0,18		S 2,28	Cl 3,12
IV	K 0,06	Ca 0,09	Sc 0,14	Ti 3+ 0,16	Mn 2+ 0,18	Fe 2+: 0,28 3+: 0,35	Co 2+ 0,28	Ni 2+ 0,34	Cu 1+: 0,32 2+: 0,48	Zn 0,36	Ga 0,24			Br 2,87
V	Rb 0,04	Sr 0,08	Y 0,07						Ag 0,53	Cd 0,40	In 0,28	Sn 2+ 0,44		I 2,56
VI	Cs 0,02	Ba 0,06	La 0,06							Hg 0,56	Tl 1+: 0,44 3+: 0,44	Pb 2+ 0,41		
VII		Ra 0,09												

TABLE 6

Comparison of the Ionic Characters of Bonds in Molecules and Solutions

Cations \ Anions	F		Cl		Br		I	
	molecule	solution	molecule	solution	molecule	solution	molecule	solution
1a	80	94	59	81	53	76	42	68
1b	52	90	24	72	18	65	12	55
2a	70	92	47	80	40	74	35	66
2b	57	90	35	72	29	65	20	55

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INVESTIGATION OF QUADRIVALENT PLUTONIUM COMPLEX FORMATION IN SULFURIC ACID SOLUTIONS

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Formation of complex plutonium ions in sulfuric acid solutions is stepwise in character. The stability of the complex ions decreases with rise of temperature. Complex sulfate ions of quadrivalent plutonium can be represented by the general formula $[Pu(SO_4)_n(H_2O)_{8-n}]^{+4-2n}$, where n may be from 1 to 8.

The formation of complex sulfate ions containing quadrivalent plutonium was studied by the method of ion transference in an electric field [1]. It was found that plutonium forms stable complex anions at relatively low concentrations of sulfuric acid. Determinations of the instability constants of the first and second plutonium sulfate complexes [2] gave $K' = (2.17 \pm 0.05) \cdot 10^{-4}$ for the first sulfate complex $PuSO_4^{2+}$ and $K'' = 2.17 \cdot 10^{-2}$ for the second sulfate complex $Pu(SO_4)_2$.

There are no data in the literature on spectrophotometric investigations of complex formation in sulfuric acid solutions.

1. Preparation of Solutions and Determination Technique

For preparation of the sulfuric acid solutions, weighed quantities of plutonium sulfate were dissolved in sulfuric acid, and the solutions were diluted with water or sulfuric acid to give the required sulfuric acid concentrations.

Plutonium sulfate was prepared by evaporation of a washed plutonium hydroxide precipitate with concentrated sulfuric acid in a platinum basin. The sulfate was calcined at 350-400° to constant weight. The substance prepared by this method has a brick-red color and exactly corresponds to $Pu(SO_4)_2$ in composition. When the precipitate is dissolved in sulfuric acid pink solutions containing plutonium in the quadrivalent state only are formed.

The absorption spectra were measured with a nonrecording quartz SF-11 spectrophotometer in the 385 to 1000 mμ region.

2. Investigation of Absorption Spectra of Plutonium Sulfate Solutions

Studies of the dependence of the optical density of the absorption bands on the plutonium concentration at constant sulfuric acid concentration showed that the optical density of all the absorption bands conforms to the Lambert-Beer law.

Figure 1 shows the form of the plutonium absorption spectra at different sulfuric acid concentrations. Table 1 gives the molar extinction coefficients ϵ, and in Fig. 2, ϵ of the plutonium absorption bands is plotted against the sulfuric acid concentration.

It follows from Table 1 and Fig. 2 that the following principal changes take place in the absorption spectrum of quadrivalent plutonium with increase of sulfuric acid concentration:

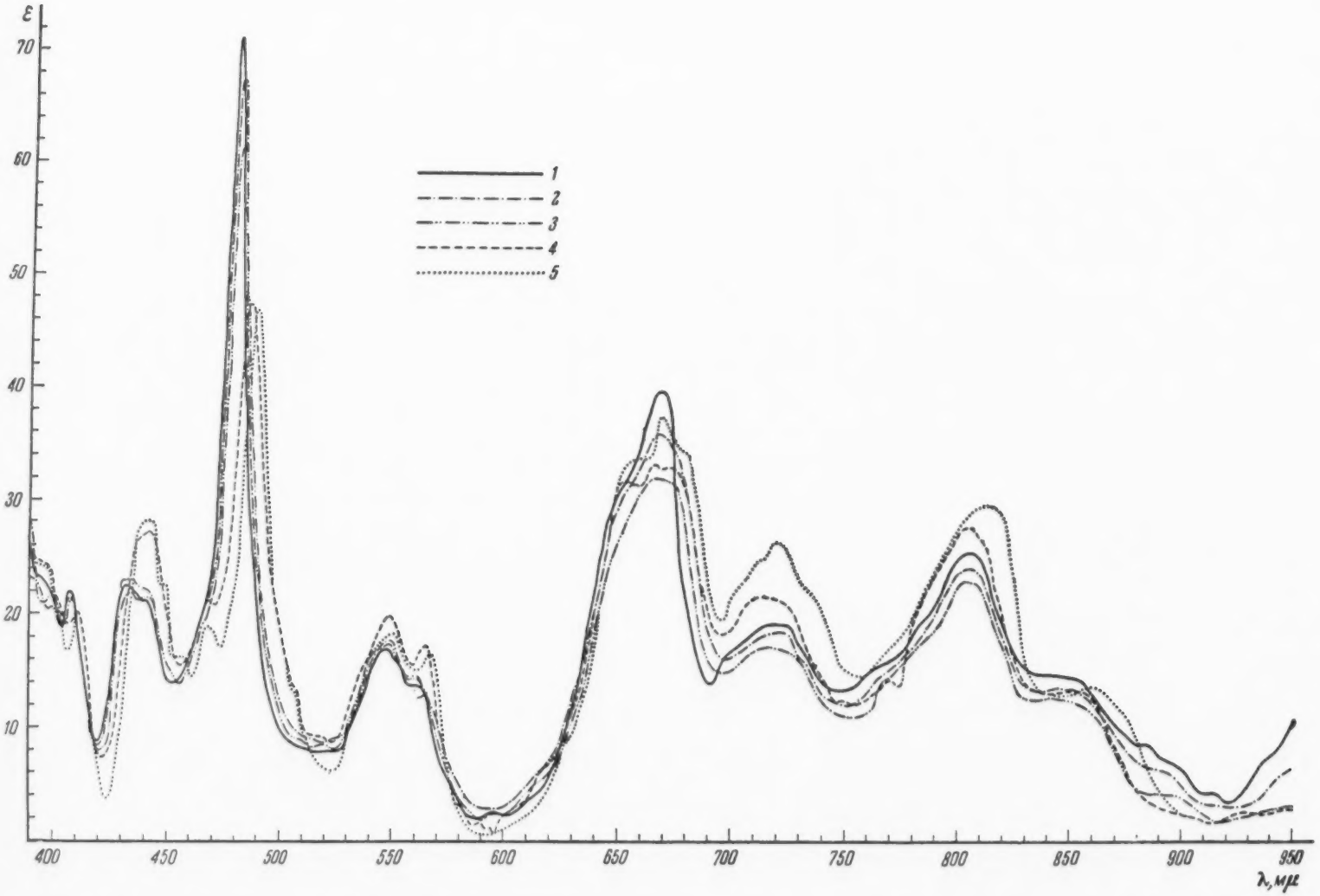

Fig. 1. Absorption spectra of quadrivalent plutonium at various concentrations of sulfuric acid: 1) 0.26 M; 2) 0.53 M; 3) 1.09 M; 4) 5.36 M; 5) 8.14 M.

TABLE 1

Molar Extinction Coefficients ε for the Maxima of the Absorption Bands of Sulfuric Acid Solutions of Quadrivalent Plutonium

Molar concentration of sulfuric acid													
0,26		0,53		1,09		2,34		3,74		5,36		8,14	
λ, mμ	ε	λ, mμ	ε	λ, mμ		λ, mμ	ε	λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
805	25,3	805	24,0	803	22,8	817,5	31,1	810	27,6	805	27,8	810	29,3
718	19,2	722	18,3	715	17,2	715	20,7	718	21,8	713	21,6	718	26,4
667,5	39,5	667,5	35,8	665	31,8	670	34,0	675	37,1	665	33,3	667,5	37,6
548	16,8	550	17,7	550	17,5	552	14,2	550	19,3	550	19,8	550	18,4
479,5	70,9	480,5	67,4	481	61,2	484	53,1	485	51,1	486,5	47,3	489	46,9
435	22,7	434,5	23,0	434	22,0	441	21,3	443	28,9	443	27,2	442	28,2
408	24,2	408,5	21,7	408	21,2	408	17,1	414	23,3	410	19,7	412	20,2

TABLE 2

Molar Extinction Coefficients ε of Absorption Bands of Quadrivalent Plutonium Solutions

Pu solution in 0.26 M H_2SO_4		Pu solution in 0.26 M H_2SO_4 + 8.5 M $(NH_4)_2SO_4$		Pu solution in 0.26 M H_2SO_4		Pu solution in 0.26 M H_2SO_4 + 8.5 M $(NH_4)_2SO_4$	
λ, mμ	ε	λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
805	25,3	807,5	28,9	479,5	70,9	489	41,7
718	19,2	715	22,9	435	22,7	444	28,7
667,5	39,5	667,5	33,5	408	24,2	413	17,5
548	16,8	548	19,9				

1. With increase of the sulfuric acid concentration from 0.26 to 5 M, the value of ε for the 480 mμ absorption band gradually decreases. Subsequent increase of concentration to 8.14 M does not lead to a decrease of ε. Simultaneously, the band maximum is shifted into the long-wave region of the spectrum (from 479.5 mμ in 0.26 M to 489 mμ in 8.14 M sulfuric acid), and the half-width of the band increases from 10 to 15 mμ.

2. The curves for ε of the absorption bands against the sulfuric acid concentration have a series of maxima and minima. It is significant that a minimum on the curve corresponds to a shift of the absorption band maximum into the short-wave region, while a maximum corresponds to a shift of the maximum into the long-wave region. The extremals on the curves for ε against the sulfuric acid concentration correspond to the following H_2SO_4 concentrations: 0.5, 1, 2.4, 3.7, and 5.3 M.

Studies of the transference of plutonium ions in sulfuric acid solutions [1] showed that in a 0.1 M sulfuric acid solution of quadrivalent plutonium 25% of the plutonium ions goes to the cathode and 75% to the anode. In 0.5 M sulfuric acid solution only 6% of the plutonium ions goes to the cathode, and 94% to the anode. In view of the fact that on the curves for the molar extinction coefficients of the absorption bands against the sulfuric acid concentrations the first extremals correspond to 0.5 M sulfuric acid, it may be supposed that formation of the third sulfate complex ion of quadrivalent plutonium $[Pu(SO_4)_3]^{2-}$ is formed in this region. Increase of the sulfuric acid concentration to 1 M leads to predominant formation of the fourth sulfate complex ion $[Pu(SO_4)_4]^{4-}$, and at sulfuric acid concentrations of 2.4, 3.7, and 5.8 M the fifth, sixth, and seventh complex plutonium ions, respectively, are formed. Increase of the sulfuric acid concentration to over 5.8 M should lead to the formation of the eighth complex sulfate ion $[Pu(SO_4)_8]^{12-}$.

This mechanism is consistent with our data for nitric acid solutions of quadrivalent plutonium [3]. It was found that the start of formation of the third nitrate complex ion $[Pu(NO_3)_8]^{+}$ is accompanied by a decrease of the molar extinction coefficient of the 480 mμ band, which continues up to the formation of the fifth nitrate complex

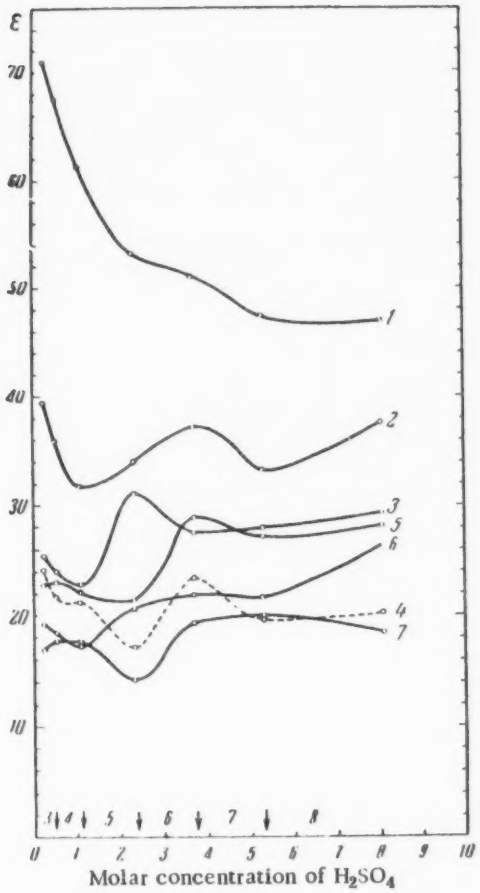

Fig. 2. Effect of sulfuric acid concentration on the molar extinction coefficients for absorption bands of quadrivalent plutonium. Absorption bands (curve numbers): 1) 480 mμ; 2) 667.5 mμ; 3) 805 mμ; 4) 408 mμ; 5) 435 mμ; 6) 718 mμ; 7) 548 mμ.

$[Pu(NO_3)_5]^-$. Subsequent formation of the sixth nitrate complex ion $[Pu(NO_3)_6]^{-2}$ leads to an increase of ε for the 480 mμ band. In the case of sulfuric acid solutions of quadrivalent plutonium, the formation of the sixth sulfate complex ion is also accompanied by some increase of ε for this absorption band, although the increase is much less than in nitric acid solutions.

Obviously, these differences in the variations of ε for similar absorption bands in consecutive formation of nitrate and sulfate complex ions of quadrivalent plutonium, respectively, can be explained by the fact that the conditions of equilibrium between different complex ions are not the same in nitric acid as in sulfuric acid solutions. Therefore, there cannot be complete similarity between the curves for ε of the absorption bands in formation of sulfate and nitrate complex ions with the same number of ligands.

Thus, as the sulfuric acid concentration increases, sulfate groups are added progressively to the plutonium ion with formation of complex ions containing up to eight sulfate groups (the regions of predominant formation of particular complex ions are indicated in Fig. 2, where the numbers between the arrows marking different regions of sulfuric acid concentration represent the number of sulfate groups contained in the corresponding complex ion).

3. Influence of Hydrogen Ions on Complex Formation in Sulfuric Acid Solutions of Plutonium

Investigations of formation of plutonium complexes in nitric acid solutions revealed the strong influence of acidity on formation of nitrate complexes of quadrivalent plutonium [3]. It was therefore of interest to study the influence of hydrogen ions on formation of sulfate complexes of quadrivalent plutonium.

We studied the effect of increasing concentration of sulfate ions in 0.26 M sulfuric acid solution containing plutonium. The sulfate concentration was raised by additions of weighed quantities of crystalline ammonium sulfate to the solution. Increase of sulfate ion concentration produces the same changes in the absorption spectrum as increase of sulfuric acid concentration, but the effect of ammonium sulfate on the absorption spectrum is much greater than the effect of increasing sulfuric acid concentration. Thus, at a sulfate concentration in 0.26 M sulfuric acid of plutonium equivalent to the sulfate concentration in 1 M solution of ammonium sulfate in sulfuric acid, the change produced in the absorption spectrum is the same as that observed when about 5 M sulfuric acid is used as the solvent. With increase of the ammonium sulfate concentration in the solution above 3 M, the molar extinction coefficient of the 480 mμ band changed very little, and at about 7 M complete "saturation" of all the absorption bands was reached, i.e., further increase of sulfate ion concentration did not produce any noticeable changes in the absorption spectrum.

Figure 3 shows the absorption spectra of quadrivalent plutonium solutions in 0.26 M sulfuric acid and in 0.26 M sulfuric acid containing 8.5 moles of ammonium sulfate per liter. The molar extinction coefficients of the absorption bands for these two solutions are compared in Table 2.

Comparison of the absorption spectrum of plutonium in 0.26 M sulfuric acid solution containing 8.5 moles

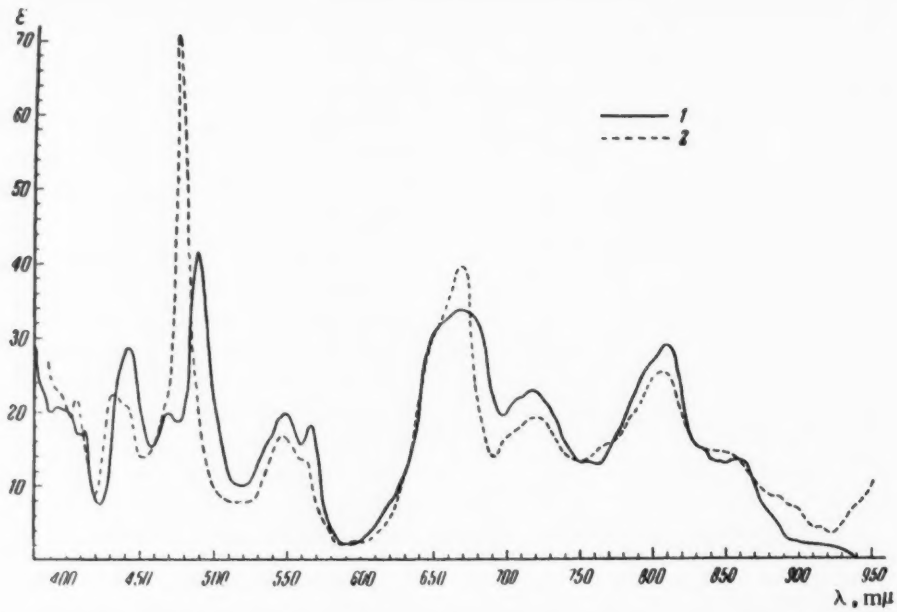

Fig. 3. Influence of ammonium sulfate on the absorption spectrum of quadrivalent plutonium solution: 1) absorption spectrum of plutonium in 0.26 M H_2SO_4 + 8.5 M $(NH_4)_2SO_4$; 2) the same, in 0.26 M H_2SO_4.

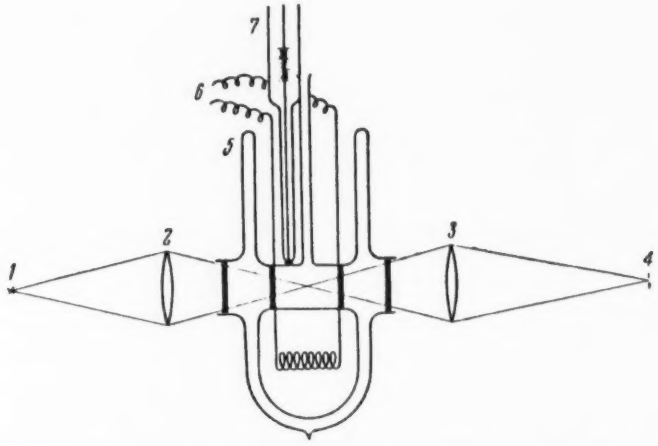

Fig. 4. Diagram of apparatus for photographic investigation of absorption spectra at various temperatures: 1) light source; 2) and 3) achromatic condensers; 4) spectrograph slit; 5) Dewar flask with sealed-in cylindrical cell; 6) Nichrome heating spiral; 7) thermometer.

of ammonium sulfate per liter with the absorption spectra of plutonium solutions in sulfuric acid leads to the conclusion that replacement of water molecules by sulfate groups in the hydrate sphere of the plutonium ion is greatest in this solution. It is highly probable that the absorption spectrum in Fig. 3 is the absorption spectrum of the complex plutonium anion in which all eight water molecules of the hydration layer are replaced by sulfate groups. This view is also probably supported by the fact that the absorption spectrum of plutonium in 0.26 M sulfuric acid containing 8.5 moles of ammonium sulfate per liter is very similar in general form to the absorption spectrum of plutonium solution in perchloric acid, where plutonium ions are in the hydrated form. The symmetry of the complex plutonium ions in solution should be the same in both these cases.

These variations in the nature of the absorption spectra of plutonium solutions, caused by increasing sulfuric acid concentration on the one hand, and by increase of the ammonium sulfate concentration at constant acidity on the other, lead to the conclusion that, in contrast to solutions of plutonium in nitric acid [3], increase of hydrogen ion concentration in sulfate solutions lowers the degree of complex formation of quadrivalent plutonium.

The formation of higher complex sulfate ions at low solution acidities is attributable to the higher stability of the sulfate complexes in comparison with the nitrate complexes. The decrease in the degree of plutonium complex formation with increase of hydrogen ion concentration is due to decrease in the concentration of sulfate ions owing to formation of bisulfate ions. Therefore, although increase of the hydrogen ion concentration does favor more extensive replacement of water molecules in the hydration sphere of the plutonium ion by sulfate ions, nevertheless, because of the decreasing concentration of sulfate ions, the degree of complex formation in sulfuric acid solutions is less than in solutions containing sulfate salts.

4. Influence of Temperature on the Stability of Quadrivalent Plutonium Complex Sulfate Ions

It is reported in the literature [4] that rise of temperature may favor complex formation in the case of plutonium, which has a small ionic radius and a high charge. It was of interest to verify this in the case of plutonium sulfate complex ions.

A solution of plutonium in 0.26 M sulfuric acid was contained in a cylindrical cell fused into a Dewar flask, so that the temperature of the solution could be kept constant or varied at will from a low level to the boiling point of the liquid which acted as a heat carrier. The solution was introduced into the cell by means of a capillary (through a long side tube), and the solution and washings were withdrawn from the cell by the same method. To heat the solution, the water around the cell was heated by means of a Nichrome spiral carrying an electric current. The water temperature was measured with an accurate thermometer graduated to an accuracy of 0.05°. The solution was kept at each given temperature for 30 min in order to establish thermal equilibrium.

The effect of temperature on the absorption spectrum of the solution was investigated photographically with the ISP-51 three-prism glass spectrograph. The line intensities were determined with the aid of the Moll K-15 recording microphotometer made by the Kipp company.

The apparatus used for photographic investigation of absorption spectra at various temperatures is shown schematically in Fig. 4. The absorption spectra of plutonium solution in 0.26 M sulfuric acid at 14, 30, 60, and 100° were first recorded, ammonium sulfate was then added, and the absorption spectra of the resultant solutions were recorded at the same temperature.

Detailed examination of the microphotometric diagrams of the 480 mμ absorption band revealed the following:

1. When a solution of plutonium in 0.26 M sulfuric acid is heated, the optical density decreases and the band shifts into the long-wave region. (These effects are very similar to the effects accompanying an increase of the degree of plutonium complex formation in sulfuric acid solutions). The half-width of the absorption band remains almost constant.

2. On addition of ammonium sulfate to the solution, the optical density of the 480 mμ absorption band decreases, the band maximum is shifted into the long-wave region, but the half-width of the band increases; with rise of temperature the optical density decreases, the band maximum is shifted into the long-wave region, and the half-width of the absorption band diminishes.

Thus, various changes are produced in the absorption spectrum when a sulfuric acid solution containing plutonium is heated and when ammonium sulfate is added (which leads to increased complex formation). This can be attributed only to a decrease in the stability of quadrivalent plutonium sulfate complex ions on heating.

It might be supposed that in individual cases the degree of complex formation may increase with rise of temperature. However, this may be caused by a decrease in the degree of hydration of the central ion, and the consequent higher probability of replacement of water molecules by the ligand, rather than by an increase in the stability of the complex with rise of temperature. Evidently, this effect can be detected most easily in complex compounds in which the ligand bond energy is much greater than the energy of the bond between the water molecule and the central ion.

SUMMARY

1. The formation of plutonium sulfate complex ions proceeds in a stepwise manner with increase of sulfuric acid concentration. The predominant formation of any particular complex ion occurs in a definite region of sulfuric acid concentrations.

2. The degree of complex formation and the stability of quadrivalent plutonium sulfate complexes decrease with rise of temperature.

3. In the formation of sulfate complex ions, the coordination number of plutonium remains unchanged and equal to the number of water molecules in the hydration sphere of the hydrated plutonium ion. Accordingly, plutonium sulfate complex ions can be represented by the formula $[Pu(SO_4)_n(H_2O)_{8-n}]^{+4-2n}$, where n may have values from 1 to 8.

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INFLUENCE OF THE STRUCTURES OF SOLID AND LIQUID PHASES ON THE SOLUBILITIES OF SALTS IN WATER

II. INFLUENCE OF ANION STRUCTURES ON SOLUBILITY IN THE SYSTEMS KSCN–KI–H_2O AND KSCN–KCl–H_2O

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In the systems investigated, the high solubility of thiocyanate (in comparison with halides) in binary and ternary solutions is due largely to differences between the structure of the SCN^- anion and the I^- and Cl^- anions. The structural characteristics of the SCN^- ion determine the relatively low stability of the short-range order of K^+ and SCN^- ions involved in crystallization of the salt from saturated solution, and the weak negative hydration effect of the anion.

A comparison of the average values of the substitution coefficients for KSCN, KI, and KCl forms the basis of an attempt to formulate certain purely qualitative concepts of the structural state of saturated solutions of these salts.

Earlier, we investigated the system KSCN–KI–H_2O [1] in order to elucidate the interaction of potassium thiocyanate and halides when dissolved together in water. In the present paper, the results of a study of the system KSCN–KCl–H_2O at 25° are given in Table 1 and Fig. 1, and solubilities in both systems are discussed in the light of the views put forward by one of us in the preceding paper [2]. For clearer comparison, Table 2 contains data on solubilities in the system KSCN–KI–H_2O at 25°.

The system KSCN–KCl–H_2O was studied by us for the first time. The compositions of the liquid and solid phases were determined by potentiometric titration of SCN^- and Cl^- ions with 0.1 N $AgNO_3$ solution, with the aid of a highly sensitive potentiometer.

The SCN^- ion and the salt KSCN are, respectively, similar to the ions Cl^-, Br^-, I^-, and to the salts formed by these ions with the K^+ ion, in a number of properties which influence solubility in various ways (energies of ion hydration, heats of solution of the salts). Despite this, however, the molality of a KSCN solution saturated at 25° is approximately three times the corresponding molality of KI, and more than five times the molality of KCl. These differences between the individual solubilities of thiocyanate and halides apparently depend significantly on anion structure and the short-range order of the ions which determines crystallization of salts from saturated solutions.

The linear SCN^- ion contains atoms differing in chemical nature. Together they form an asymmetric group in which carbon occupies the central position, while the nitrogen and sulfur atoms play the role of packing spheres in the thiocyanate crystal structure [3]. According to earlier work on x-ray structural analysis of KSCN crystals [4], the thiocyanate ion has the structure $\overline{S} - C \equiv N$. Later work [5,6] showed that the structure is $S = C = \overline{N}$; this is confirmed by the presence of stable N – H ... N hydrogen bonds in NH_4SCN crystals [5], due to the negative charge on the nitrogen, and also by other physicochemical properties of thiocyanates.

TABLE 1

The System KSCN–KCl–H_2O at 25°

Points No.	Composition of solution						K	Comp. of residue		Solid phase
	wt.%			moles/ 1000 g water				wt.%		
	KSCN	KCl	H_2O	KSCN	KCl	total		KSCN	KCl	
1	—	26,56	73,44	—	4,85	4,85	—	—	—	KCl
2	4,39	24,09	71,52	0,63	4,52	5,15	0,73	—	—	the same
3	8,01	22,07	69,92	1,17	4,23	5,40	0,73	1,49	80,54	»
4	9,58	21,25	69,17	1,43	4,12	5,55	0,72	—	—	»
5	13,05	19,66	67,29	1,99	3,92	5,91	0,69	—	—	»
6	20,14	15,84	64,02	3,23	3,31	6,54	0,70	3,7	80,13	»
7	24,30	13,80	61,90	4,04	2,99	7,03	0,68	—	—	»
8	29,18	11,96	58,86	5,10	2,72	7,82	0,65	—	—	»
9	33,95	10,01	56,04	6,23	2,39	8,62	0,64	4,52	86,47	»
10	37,87	8,49	53,64	7,27	2,13	9,40	0,62	—	—	»
11	43,47	6,64	49,89	8,96	1,78	10,74	0,60	—	—	»
12	49,09	4,90	46,01	10,98	1,43	12,41	0,57	12,13	74,75	»
13	52,67	4,15	43,18	12,55	1,30	13,85	0,55	—	—	»
14	55,71	3,44	40,85	14,03	1,13	15,16	0,54	—	—	»
15	56,09	3,35	40,56	14,23	1,11	15,34	0,54	—	—	»
16	59,17	2,85	37,98	16,04	1,00	17,04	0,52	—	—	»
17	62,48	2,39	35,13	18,30	0,91	19,21	0,50	23,98	62,00	»
18	65,47	2,00	32,53	20,72	0,83	21,55	0,49	—	—	»
19	69,59	1,62	28,79	24,87	0,76	25,63	0,47	79,21	11,92	KCl + +KSCN
20	71,10	—	28,90	25,33	—	25,33	—	—	—	KSCN

TABLE 2

The System KSCN–KI–H_2O at 25°

Points No.	Composition of solution						K	Comp. of residue		Solid phase
	wt.%			moles/ 1000 g water				wt.%		
	KSCN	KI	H_2O	KSCN	KI	total		KSCN	KI	
1	—	59,42	40,58	—	8,82	8,82	—	—	—	KI
2	5,04	55,29	39,67	1,31	8,40	9,71	0,48	—	—	the same
3	13,65	48,08	38,27	3,67	7,57	11,24	0,49	3,07	87,80	»
4	21,83	41,23	36,94	6,08	6,72	12,80	0,49	—	—	»
5	29,51	34,73	35,76	8,49	5,85	14,34	0,49	6,37	86,94	»
6	37,00	29,49	33,51	11,36	5,30	16,66	0,47	11,53	78,11	»
7	44,00	24,25	31,75	14,26	4,60	18,86	0,47	—	—	»
8	49,83	20,95	29,22	17,56	4,31	21,87	0,45	8,78	85,92	»
9	53,16	18,58	28,26	19,36	3,96	23,32	0,45	—	—	»
10	55,70	16,97	27,33	20,97	3,73	24,70	0,45	13,62	79,54	»
11	58,37	15,55	26,08	23,04	3,60	26,64	0,44	67,01	25,72	+KSCN
							1,40	56,69	37,19	
12	60,46	12,87	26,67	23,32	2,89	26,21	1,43	85,25	4,77	KSCN
13	63,45	9,38	27,17	24,03	2,10	26,13	1,39	—	—	the same
14	65,61	6,72	27,67	24,39	1,45	25,84	1,43	—	—	»
15	67,06	4,72	28,22	24,25	0,99	25,44	1,50	90,72	1,38	»
16	71,10	—	29,90	25,33	—	25,33	—	—	—	»

In the KSCN crystal, each ion is surrounded by eight neighboring oppositely charged ions situated at the corners of a distorted cube.

Geometrical analysis of the structure of KSCN [4] shows that SCN^- ions surround the potassium ion in two groups, each consisting of four like atoms, without alternation of sulfur and nitrogen atoms. The ionic bond effected by the nitrogen ends of the thiocyanate ion is more stable than bonds effected by sulfur atoms. The ion packing in the KSCN crystal has low symmetry and, in view of the asymmetry of the ionic charge, weak ionic bonding.

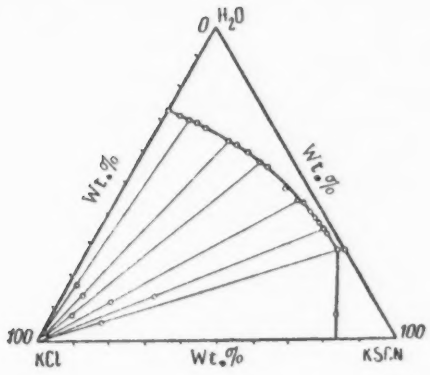

Fig. 1.

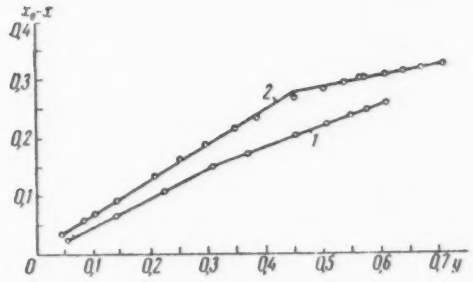

Fig. 2. Variation of $x_0 - x$ with y for ternary solutions saturated with KI (1) in the system KSCN–KI–H_2O, and saturated with KCl (2) in the system KSCN–KCl–H_2O.

KCl and KI crystals belong to the cubic system. The packing of large spherical ions in them corresponds to the structural type of sodium chloride. The interionic distances in KCl and KI crystals are 3.139 and 3.526 A, respectively [7].

Comparison of the features of the crystal structure of KSCN with those of KCl and KI shows that the short-range order of K^+ and SCN^- ions which arises in KSCN solutions as the result of electrostatic interaction is less stable than the short-range order which arises in the same way in KCl and KI solutions. In the light of the structural approach to solubility, this means that thermal motion and water molecules prevent the formation of an effective structure to a much greater extent during dissolution of KSCN than during dissolution of KCl and KI. The appreciable difference between the solubilities of KCl and KI can also be attributed to stability differences between the structural combinations of ions which cause crystallization from solution.

The higher saturation concentrations of KSCN as compared with KCl and KI are also associated with differences in the action of the anions on the structure of water in the solution. The low effect of the action of SCN^- anions on the structure of the solvent water is probably determined, to a great extent, by incorporation of these ions in the electrically neutral channels in the water structure. Linear ions can be accommodated much more conveniently in the channels between the water molecules than in the tetrahedral water cell itself [8]; this was demonstrated for the uranyl ion [9,10]. In the case of the SCN^- ion, it may be assumed that formation of an interstitial structure is favored by the configuration of the ion and by the asymmetry of its ionic charge. In the anionic group in question, sulfur is approximately electroneutral, while the nitrogen can form N ... HO hydrogen bonds, but with water molecules. Therefore, distribution of SCN^- ions in water should not lead to any significant disturbance in the structure of the water itself; this cannot be assumed if water molecules are replaced by thiocyanate ions, in view of their low symmetry and large linear extent. It may be assumed that when KSCN dissolves, substitutional and interstitial structures are retained up to a concentration approximately corresponding to the boundary of complete solvation [11] of the ions, so that high equilibrium concentrations can be reached. In contrast to SCN^-, I^- and Cl^- ions break down the structure of the solution water more or less intensively. Therefore, the influence of anions on the solubility of KI and KCl, by modification of the solvent water structure, is approximately opposite in character to the corresponding influence of the SCN^- anion on the solubility of KSCN.

Joint solubility in the two systems KSCN–KI–H_2O and KSCN–KCl–H_2O is characterized by a linear relationship between $x_0 - x$ and y; this relationship is represented by two straight lines differing in slope for ternary solutions saturated with respect to KCl and KI. The upper and lower straight lines for KCl and KI (Fig. 2) are drawn through points calculated from the compositions of ternary solutions corresponding to points 2-10 and 11-19 in Table 1, and 2-5 and 6-12 in Table 2, respectively. The average values of K are: 0.68 for the lower and 0.53 for the upper straight lines of the KCl plot; 0.49 for the lower and 0.45 for the upper straight lines of the KI plot, and 1.43 for KSCN in the system KSCN–KI–H_2O. Tables 1 and 2 show that the molality of KSCN in eutonic solutions of the two systems is only a little lower than the molality of the saturated binary solution, whereas the corresponding lowering for KCl and KI is greater. The molality ratio characterizing the solubilities of KCl and KI in pure water, and the respective eutonic solutions, is 6.38 for the first salt and 2.45 for the second. This kind of decrease of individual solubilities is, to some extent, due to the fact that the stability of short-range order of the ions involved in crystallization increases in the sequence KSCN, KI, and KCl. Accordingly, the

concentration range of ternary solutions saturated with KSCN is much narrower in the system KSCN–KI–H_2O, and quite negligible in the system KSCN–KCl–H_2O, by comparison with the concentration range of ternary solutions for the univariant KI and KCl curves. The high solubility of KSCN in eutonic solutions is also caused by the retarding effect of the unlike I^- and Cl^- anions on the formation of a structure effective with respect to KSCN in the corresponding ternary solutions. The fact that such a structure arises in eutonic solutions when their molalities with respect to KSCN differ little from the molality of a saturated binary KSCN solution indicates the lower stability of the short-range order of K^+ and SCN^- ions, and the possible formation of hydrogen bonds between SCN^- ions and water molecules. The appreciable difference between the solubilities of KI and KCl in eutonic solutions of the corresponding systems is probably due to the fact that thermal motion in solution weakens the attraction forces between K^+ and I^- ions to a greater extent than between K^+ and Cl^- ions.

The fairly large difference between the substitution coefficients for KSCN and KI in the system KSCN–KI–H_2O, and the break in the $x_0 - x$ curve as a function of y for KI, are also determined, to some extent, by the structural state of the corresponding saturated binary and ternary solutions.

Dissolution of increasing amounts of KSCN in saturated KI solution is accompanied by a comparatively small relative degree of salting out of the saturating salt, so that a high KSCN concentration is reached in the eutonic solution. This feature of the joint solubility is consistent with the concept that the structure of a saturated solution has a relatively large region of joint order of ions and water molecules, and a relatively small region of ionic short-range order. It is also likely that the part of the structure effective with respect to KI is disturbed little with increase of the concentration of the nonsaturating salt KSCN in ternary solutions, in view of the slight decrease of the average value of K for the upper portion of the graph for $x_0 - x$ as a function of y in comparison with the average value of K for the lower portion. This hypothesis is consistent with the low probability of replacement of I^- ions by SCN^- ions in the effective part of the structure of the solution saturated with KI. It is more probable that the ions of the nonsaturating salt KSCN would be predominantly located in the region of the saturated solution enriched with water.

When a KSCN concentration approximately corresponding to the break on the $x_0 - x = f(y)$ curve is reached in ternary solutions saturated with KI, the structure of ternary solutions becomes more closely packed than the structure of a binary saturated KI solution. The short-range order characteristic of concentrated KSCN solutions predominates in a more closely packed structure of this type. Therefore, joint solubility in ternary solutions corresponding to the lower linear portion of the graph for KI is determined by the predominant influence of the original structure of the saturated KI solution, while in ternary solutions corresponding to the upper linear portion, both the original and the modified structure exert an influence. The substantial increase of the average value of the substitution coefficient for KSCN over the corresponding value for KI depends on the difference between the structures of the respective saturated salt solutions. It may be assumed that the over-all short-range order in the structure of saturated KSCN solution approaches, to the greatest possible extent, to the order characteristic of the salt, since, in such a solution, there is, on the average, one water molecule per ion. Therefore, the relatively high salting-out effect of KI on KSCN is probably determined to a considerable extent by the existence, in saturated KSCN solution, of a relatively large region of short-range order of ions which is capable of crystallization.

The average values of K for KI and KCl do not differ significantly in the systems studied. The relatively small difference between the values of K and the similar character of joint solubility by the KCl and KI univariant curves are due to the structural similarity between saturated binary solutions of the two salts, and the approximately equal changes in ternary solutions with a considerable increase of the KSCN concentration. It may be assumed that in KCl and KI solutions saturated at 25°, joint order of ions and water molecules prevails; in the case of saturated KCl solution, this consists primarily of the short-range order characteristic of water. This kind of structural heterogeneity was established by Shakhparonov [12] for saturated KCl solutions at temperatures up to 22°.

The greater decrease of the average value of K of the upper portion of the $x_0 - x = f(y)$ curve in comparison with the lower portion, which is found in the case of KCl as compared with KI, is due to the appreciable decrease of the KCl concentration in ternary solutions as the eutonic point is approached. Decrease of the KCl concentration diminishes the region of structure effective with respect to KCl in ternary solutions, and this is the cause of the decrease in the relative salting-out of the saturating salt.

The KSCN molalities in ternary solutions corresponding to the breaks in the KCl and KI graphs are 8.64 and 8.49, respectively. The closeness of these values confirms the approximately similar character of the structural changes in saturated binary KCl and KI solutions as they pass into ternary solutions with considerable increases in the concentration of the nonsaturating salt.

SUMMARY

1. Solubility in the system KSCN–KCl–H_2O at 25° was studied. As in the KSCN–KI–H_2O system studied previously, the components do not form chemical compounds or solid solutions.

2. Solubilities in the systems KSCN–KI–H_2O and KSCN–KCl–H_2O were correlated with the structures of the component salts and of their saturated solutions.

3. The significant difference between the solubilities of thiocyanate and halides in the two systems is largely determined by structural differences between the SCN^- anion and the I^- and Cl^- anions.

4. The high solubility of KSCN in binary and ternary solutions, in comparison with KI and KCl, is due to the relatively low stability of the short-range order of K^+ and SCN^- ions involved in crystallization and to the weak negative hydration of the SCN^- anion.

5. Comparison of the average values of the substitution coefficients for KSCN, KI, and KCl forms the basis of certain purely qualitative concepts of the structural state of saturated solutions of these salts.

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INFLUENCE OF THE STRUCTURES OF SOLID AND LIQUID PHASES ON THE SOLUBILITIES OF SALTS IN WATER

III. INFLUENCE OF ANION STRUCTURES ON SOLUBILITY IN THE SYSTEMS $KNO_2-KCl-H_2O$ AND $KNO_2-KSCN-H_2O$

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The high solubility of KNO_2 in binary and ternary solutions of the systems $KNO_2-KCl-H_2O$ and $KNO_2-KSCN-H_2O$ is explained in the light of the structural characteristics of the NO_2^- anion. Consideration of experimental data for the system $KNO_2-KCl-H_2O$ from the structural standpoint shows that formation of solid solutions based on KNO_2 involves partial replacement of NO_2^- ions by Cl^- ions in the region of short-range order of K^+ and NO_2^- ions capable of crystallization from ternary solutions in accordance with the univariant KNO_2 curve. It follows from data on joint solubility in the $KNO_2-KSCN-H_2O$ system that the transition of the structure of ternary solutions to closer packing, with simultaneous presence of NO_2^- and SCN^- ions, favors the attainment of very high salt concentrations in the liquid phase.

Earlier we investigated the system $KNO_2-KCl-H_2O$ at 25 and 40°, and demonstrated the formation of solid solutions in accordance with the univariant KNO_2 curve [1]. In the present paper we give the results of a study of the system $KNO_2-KSCN-H_2O$ at 25° in Table 1 and Fig. 1, and correlate solubilities in both systems with the structures of the salts and of their saturated solutions. Accordingly, solubility data for the system $KNO_2-KCl-H_2O$ at 25° are given in Table 2.

The system $KNO_2-KSCN-H_2O$ was studied for the first time. The liquid and solid phase compositions were found from the results of quantitative determinations of SCN^- and K^+ ions. Potentiometric titration with 0.1 N $AgNO_3$ solution was used for determination of SCN^-, and K^+ was determined by the sulfate method.

The component salts in the systems $KNO_2-KCl-H_2O$ and $KNO_2-KSCN-H_2O$ differ in the structures of the unlike anions. In the first system, the molality of a KNO_2 solution saturated at 25° is more than eight times the molality of a saturated KCl solution, whereas, in the second system, the difference is relatively small, as both the component salts have high individual solubilities. Therefore, investigations of the influence of the structural factor on solubility in the systems $KNO_2-KCl-H_2O$ and $KNO_2-KSCN-H_2O$ must, to a certain extent, be based on a consideration of the differences between the anion structures. The structures of anions determine, to a considerable extent, their influence on the structure of solvent water and the relative stability of the short-range order of the ions involved in crystallization which arises in solution.

The KNO_2 crystal contains angular NO_2^- ions with O–N–O bond angles of 132° and N–O and O–O distances of 1.14 A and 2.08 A, respectively [2]. The monoclinic KNO_2 lattice can be derived from the lattice of the sodium chloride type [3]. When the spherically symmetrical chloride ion in the NaCl lattice is replaced by the angular NO_2^- ion, the symmetry of the resultant $NaNO_2$ becomes rhombic. Replacement of Na^+ ions by K^+ ions

TABLE 1

The System KNO_2–KSCN–H_2O at 25°

Points No.	Composition of solution wt.%			moles/1000 g water			K	Comp. of residue wt.%		Solid phase
	KNO_2	KSCN	H_2O	KNO_2	KSCN	Сумма		KNO_2	KSCN	
1	76,16	—	23,84	37,54	—	37,54	—	—	—	KNO_2
2	71,56	5,61	22,83	36,84	2,53	39,17	0,93	—	—	»
3	67,14	10,87	21,99	35,88	5,09	40,97	0,95	—	—	»
4	62,47	15,89	21,64	33,92	7,56	41,48	0,98	87,09	5,73	»
5	59,46	20,51	20,03	34,89	10,53	45,42	0,93	—	—	»
6	54,50	27,38	18,12	35,34	15,55	50,89	0,90	—	—	»
7	50,82	33,20	15,98	37,38	21,38	58,76	0,87	80,81	12,85	»
8	45,21	40,52	14,27	37,23	29,22	66,45	0,87	59,96	36,56	KNO_2 +
							0,59	34,71	61,64	+ KSCN
9	40,17	43,87	15,96	29,56	28,29	57,85	0,59	—	—	KSCN
10	32,46	48,93	18,61	20,49	27,07	47,56	0,59	—	—	»
11	27,85	51,82	20,33	16,09	26,23	42,32	0,60	7,60	86,03	»
12	22,44	55,34	22,22	11,87	25,63	37,50	0,61	—	—	»
13	18,12	58,73	23,15	9,20	26,11	35,31	0,59	—	—	»
14	13,22	62,20	24,58	6,32	26,04	32,36	0,57	5,08	85,81	»
15	8,41	65,05	26,54	3,72	25,24	28,96	0,61	—	—	»
16	3,68	68,08	28,24	1,53	24,75	26,28	0,67	—	—	»
17	—	70,83	29,17	—	24,99	24,99	—	—	—	»

TABLE 2

The System KNO_2–KCl–H_2O at 25°

Points No.	Composition of solution wt.%			moles/1000 g water			K	Comp. of residue wt.%		Solid Phase
	KNO_2	KCl	H_2O	KNO_2	KCl	total		KNO_2	KCl	
1	—	26,44	73,56	—	4,83	4,83				KCl
2	5,04	23,77	71,19	0,83	4,48	5,31	0,61			The same
3	9,63	21,63	68,74	1,64	4,22	5,86	0,58	2,58	80,01	»
4	13,56	19,29	67,15	2,37	3,86	6,23	0,60	—	—	»
5	20,60	17,00	62,40	3,88	3,65	7,53	0,52	—	—	»
6	25,44	14,66	59,90	4,99	3,51	8,50	0,52	—	—	»
7	30,59	12,49	56,92	6,31	2,93	9,24	0,52	7,57	82,01	»
8	35,98	9,71	54,31	7,79	2,39	10,18	0,53	—	—	»
9	44,08	8,03	47,89	10,79	2,25	13,04	0,48	—	—	»
10	50,71	6,31	42,98	13,87	1,98	15,85	0,45	—	—	»
11	55,57	5,12	39,31	16,61	1,76	18,37	0,44	7,07	88,37	»
12	59,85	4,28	35,87	19,60	1,59	21,19	0,42	—	—	»
13	66,20	3,41	30,39	25,60	1,51	27,11	0,40	10,93	84,37	»
14	66,60	3,16	30,24	25,86	1,39	27,25	0,40	44,06	47,51	KCl +
								50,76	40,63	+ K(NO_2, Cl)
							2,55	67,32	21,03	The same
15	67,70	2,66	29,64	26,88	1,22	28,10	2,61	76,83	14,14	K(NO_2, Cl)
16	69,72	1,86	28,42	28,82	0,88	29,70	2,80	83,03	10,70	The same
17	72,15	1,24	26,61	31,87	0,64	32,51	2,41	84,77	5,74	»
18	74,23	0,69	25,08	34,77	0,36	35,13	1,89	87,96	2,73	»
19	75,65	—	24,31	36,57	—	36,57	—	—	—	KNO_2

in the $NaNO_2$ structure lowers the crystal symmetry further from rhombic to monoclinic in KNO_2. The structural units of the crystal, K^+ and NO_2^- ions, have a mutual coordination number of five [3]. The coordination number of the K^+ ion with respect to its surrounding oxygen atoms of five anionic groups is six [2]. The maximum K–O distance is 3.03 A, and the average K–O distance is 2.82 A [2]. Combined packing of K^+ and NO_2^- ions leads to an unstable low-symmetrical configuration of the coordination sphere, of the type of a strongly deformed octahedron. The crystal structures of KSCN and KCl are described in the previous communication [4].

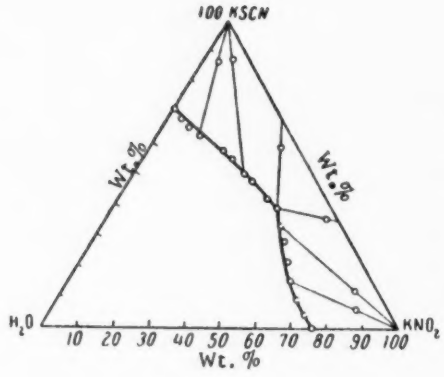

Fig. 1.

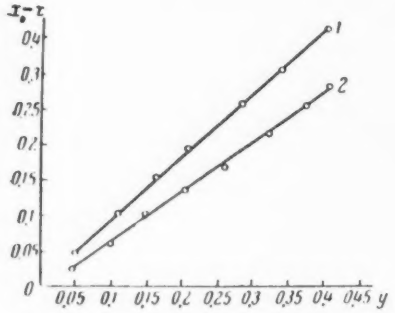

Fig. 2. The system $KNO_2-KSCN-H_2O$. Relationship between x_0-x and y for ternary solutions saturated with KNO_2 (1) and KSCN (2).

It follows from the high solubility of KNO_2, in conjunction with the crystal data given for this salt, that, in aqueous KNO_2 solutions, thermal motion and water molecules have a considerable retarding effect on the formation of short-range order of ions capable of crystallization. Therefore, an effective structure in dissolution of KNO_2 can arise only at high concentrations of the saturated solutions.

In addition to a lowered stability of the short-range order of K^+ and NO_2^- ions, the pronounced ability of the NO_2^- ion to form hydrogen bonds with water molecules in solution has a significant influence on the attainment of high equilibrium concentrations in dissolution of KNO_2. According to A. F. Kapustinskii [5], mobile hydrogen bonds between anions and water molecules in solution constitute a specific feature of their hydration. This type of hydrogen bonding has been demonstrated spectroscopically both in dilute and in concentrated aqueous solution [6] for a number of anions, including NO_3^-. The NO_2^- anion contains two negatively charged oxygen atoms and a trivalent nitrogen atom with an unshared pair of electrons [7,8]. In these states, not only the oxygen atoms, but possibly also the nitrogen atom, is capable of donor–acceptor interaction with the proton of the water molecule, which is the current explanation of the nature of the hydrogen bond [9].

It is likely that stable hydrogen bonds between NO_2^- anions and water molecules favor the predominance of a combined order of ions and water molecules in KNO_2 solutions over a considerable range of moderate concentrations, despite the fact that the angular NO_2^- ion, like the NO_3^- ion, apparently exhibits pronounced negative hydration. In solutions of higher concentration, the water molecules, still bound to the NO_2^- ions and situated among the ions constituting the salt structure, prevent crystallization and favor the attainment of a high saturation concentration.

Joint solubility in the $KNO_2-KCl-H_2O$ system is characterized by a linear relationship between x_0-x and y; for ternary solutions saturated with KCl, this relationship is represented by two straight lines of different slope, which intersect at a break point. The average value of K is 0.55 for the lower, and 0.47 for the upper linear portion of the KCl line, and 2.45 for the KNO_2 line. The values of K given in Table 2 for ternary solutions saturated with KNO_2 differ appreciably from each other. However, the deviations of these values from the mean value of 2.45 are not outside the limits of analytical error.

The mutual influence of the salts in the system $KNO_2-KCl-H_2O$ on their joint solubility for the univariant KCl curve is, in general, similar to the influence of the salts in the system $KSCN-KCl-H_2O$ on the corresponding solubility. The fairly high relative salting out of the saturating salt, characteristic of joint solubility for the univariant KNO_2 curve, is determined (apart from other factors), by a predominance of short-range ionic order capable of crystallization in the structure of saturated binary KNO_2 solution. The effectiveness of the short-range ionic order which arises in a saturated KNO_2 solution is retained on partial substitution (in ternary solutions) of Cl^- ions for NO_2^- ions, leading to crystallization of solid solutions. This substitution, which does not lead to disorder, is justified in the structural sense if we take into account the loose packing and the low symmetry of the short-range order of K^+ and NO_2^- ions, and the similarity of the K–O distance in KNO_2 to the K–Cl distance in KCl. Rapid crystallization of KNO_2 from ternary solutions, determined, to a certain extent, by formation of solid solutions, leads to an appreciable decrease in the molality of a saturated binary KNO_2 solution in a eutonic solution of the $KNO_2-KCl-H_2O$ system.

The component salts of the system $KNO_2-KSCN-H_2O$ contain anions differing in structure, the influence of which on the solubilities of the corresponding salts is generally similar if we take into account the lowered stability of ionic short-range order in the KNO_2 and KSCN structures, and the ability of both anions to form fairly stable hydrogen bonds with water molecules in solution. Because of the high individual solubilities of KNO_2 and KSCN, joint solubility in the system $KNO_2-KSCN-H_2O$ differs considerably in the mutual influence of the salts from solubility in the system $KNO_2-KCl-H_2O$.

As Fig. 2 shows, the relationship between $x_0 - x$ and y for both salts in the system $KNO_2-KSCN-H_2O$ is represented by straight lines without breaks. The average values of K, calculated from the data in Table 1, for KNO_2 and KSCN are 0.92 and 0.60. Few of the deviations of K from the mean value are outside the limits of analytical error.

Variations of the individual solubility of KNO_2 in ternary solutions of the system $KNO_2-KSCN-H_2O$ with concentration are not uniform. At relatively low concentrations of the nonsaturating salt there is, in general, an appreciable decrease in the molality of the equilibrium KNO_2 concentrations in ternary solutions relative to the molality of the binary saturated solution. This decrease in the concentration of the saturating salt ends approximately in a solution of 7.56 molality in respect to KSCN (Table 1, point 4). Over the remaining region of the univariant curve adjacent to the eutonic point the molalities of ternary solutions with respect to both salts increase in such a manner that, in a eutonic solution, the molality of KNO_2 is hardly lower, while the molality of KSCN is considerably higher than the corresponding concentrations for the individual solubilities of the salts in water. Joint solubility along the KSCN univariant curve is characterized by a continuous increase of KSCN molality in the ternary solutions relative to the molality of the binary solution. This feature of the joint solubility in the system $KNO_2-KSCN-H_2O$ confirms the view that the structural ionic groupings which cause crystallization of KNO_2 and KSCN from solutions are of lower stability, and also indicates the considerable increase of the solvent power of water in ternary solutions.

It is likely that as the particles become more closely packed in the liquid phase the disruptive effect of the water molecules on the forming salt structures is intensified. Moreover, an increase of the solvent power of water is favored by the simultaneous presence of NO_2^- and SCN^- ions, differing from each other in configuration, in the ternary solution structure.

Mutual replacement of dissimilar anions during thermal motion in the relatively closely packed structure of saturated ternary solutions leads to partial disordering of the short-range ionic order characteristic of the salts. This disordering influences the solubilities of the salts saturating the ternary solutions by decreasing the effective value of the degree of short-range ionic order arising in the saturated solution of each salt. This, in turn, leads to the relative salting out which is accompanied by the changes in the individual solubilities of the salts as described above. In the case of solubility in ternary solutions of nonsaturating salts, the disordering retards formation of short-range ionic order capable of crystallization. Therefore, increases in the concentrations of nonsaturating salts in ternary solutions for each of the univariant curves in the system $KNO_2-KSCN-H_2O$ are accompanied either by a continuous increase in the molality of the saturating salt (as in the case of KSCN), or by an increase after a certain decrease, as in the case of KNO_2. The structures effective with respect to the nonsaturating salts are formed in the eutonic solution when its total molality is appreciably higher than the sum of the molalities of the unsaturated binary solutions. It follows from the solubilities of the salts in the eutonic solutions that the retarding effect of NO_2^- ions on crystallization of KSCN from ternary solutions is stronger than the retarding effect of SCN^- ions on crystallization of KNO_2.

The comparatively low relative salting out of salts of the system $KNO_2-KSCN-H_2O$ from ternary solutions is somewhat unexpected, in view of the values of K for KNO_2 and KSCN in the systems $KNO_2-KCl-H_2O$ and $KSCN-KI-H_2O$. Apparently, the values of K for both salts in the $KNO_2-KSCN-H_2O$ system reflect the decrease (under the influence of the disordering produced by the dissimilar anions) of the regions of effective structures in the transition from binary to ternary saturated solutions. This also explains the higher value of K for KNO_2 in comparison with KSCN, if we take into account the distinction, noted above, in the action of NO_2^- and SCN^- anions on the short-range ionic order of the corresponding salts.

SUMMARY

1. Solubilities in the system $KNO_2-KSCN-H_2O$ at 25° were studied. It was found that the components do not form chemical compounds or solid solutions.

2. The high solubility of KNO_2 in binary and ternary solutions of the systems $KNO_2-KCl-H_2O$ and $KNO_2-KSCN-H_2O$ is interpreted in the light of the structural characteristics of the NO_2^- anion.

3. Formation of solid solutions based on KNO_2 in the system $KNO_2-KCl-H_2O$ is due to partial replacement of NO_2^- ions by Cl^- ions in the region of short-range order of K^+ and NO_2^- ions, which is capable of crystallization from ternary solutions in accordance with the invariant KNO_2 curve.

4. It follows from data on joint solubilities in the system $KNO_2-KSCN-H_2O$ that transition of the structures of ternary solutions to closer packing, and the simultaneous presence of NO_2^- and SCN^- ions in them favor the attainment of very high salt concentrations in the liquid phase.

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X-RAY INVESTIGATION OF FERRITES IN THE SYSTEMS $MgO - MnO - Fe_2O_3$, $MgO - Cr_2O_3 - Fe_2O_3$, and $MgO - Al_2O_3 - Fe_2O_3$

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Original article submitted February 28, 1959

The phase composition of magnesium–manganese, magnesium–chromium, and magnesium–aluminum ferrites was investigated by x-ray structural analysis. The regions of formation of one-phase solid solutions in the systems $MgO–MnO–Fe_2O_3$ (specimens annealed for 2 hr in nitrogen at 1300°) and $MgO–Cr_2O_3–Fe_2O_3$ (specimens fired at the same temperature for 2 hr in air), were determined.

When ferrites of the system $MgO–Al_2O_3–Fe_2O_3$ were sintered for 3 hr in air at 1300°, formation of one-phase solid solutions was not observed; this indicates that ferrites of this group must be heat-treated at higher temperatures.

Introduction

In recent years, new magnetic materials, ferrites, of the general formula $MeFe_2O_4$ (where Me is a bivalent metal Ni, Mn, Mg, Co, Zn, etc.), have come into very extensive use in the most diverse branches of electronics, especially in the super high-frequency range. These ferrites have cubic crystal structure of the spinel $MgAl_2O_4$ type. A close connection between the structure and magnetic properties of ferrites has been established by a number of investigations (for example, see [1]). For example, it has been shown that ferromagnetic spinels have a structure of the inverted spinel type, whereas nonferromagnetic spinels have the normal spinel structure.

Complex three- and four-component spinels are of special interest in super high-frequency electronics. Nickel–zinc ($NiO–ZnO–Fe_2O_3$), manganese–zinc ($MnO–ZnO–Fe_2O_3$), and other ferrites have accordingly been studied. It was found that the properties of ferrites (for example, the initial magnetic permeability) depend significantly on the phase composition: the initial magnetic permeability increases sharply on formation of a one-phase solid solution. Accordingly, considerable interest attaches to studies of the phase composition of ferrites, whereby it is possible, first and foremost, to find the regions in the three-component diagrams where ferrites with the desired properties should be sought. A number of studies of the phase composition of three-component ferrites (the systems studied included $MnO–ZnO–Fe_2O_3$ [2], $NiO–ZnO–Fe_2O_3$, and $CuO–ZnO–Fe_2O_3$ [3], etc.), confirmed the need for x-ray phase analysis of complex ferrites.

In the present investigation, the x-ray diffraction method was used for studying the systems $MgO–MnO–Fe_2O_3$ and $MgO–Cr_2O_3–Fe_2O_3$, and $MgO–Al_2O_3–Fe_2O_3$, since a number of ferrites from these systems are already in practical use.

Magnesium – Manganese Ferrites

Magnesium–manganese ferrites were prepared by the oxide method; the starting materials were the oxides Fe_2O_3, MgO, and MnO_2 (all of the analytical reagent grade). Manganese dioxide was reduced to manganous oxide MnO in hydrogen at 800° before use as the third ferrite component. The components were mixed in the required proportions, the mixture was heated in air at 1100° for 2 hrs, ground, molded (with paraffin), and annealed for 2 hours in thoroughly purified and dried nitrogen at 1300°.

Compositions of Ferrites Chosen for Studies in the System $MgO-MnO-Fe_2O_3$ (in molar %)

No. on diagram	MgO	MnO	Fe_2O_3	No. on diagram	MgO	MnO	Fe_2O_3	No. on diagram	MgO	MnO	Fe_2O_3	No. on diagram	MgO	MnO	Fe_2O_3
1	80	10	10	14	50	30	20	27	60	5	35	40	20	30	50
2	70	20	10	15	40	40	20	28	55	10	35	41	10	40	50
3	60	30	10	16	30	50	20	29	60	—	40	42	—	50	50
4	50	40	10	17	20	60	20	30	55	5	40	43	40	—	60
5	40	50	10	18	10	70	20	31	50	10	40	44	30	10	60
6	30	60	10	19	10	65	25	32	40	20	40	45	20	20	60
7	20	70	10	20	60	10	30	33	30	30	40	46	10	30	60
8	10	80	10	21	55	15	30	34	20	40	40	47	—	40	60
9	55	30	15	22	50	20	30	35	10	50	40	48	30	—	70
10	40	45	15	23	40	30	30	36	—	60	40	49	20	10	70
11	70	10	20	24	30	40	30	37	50	—	50	50	10	20	70
12	60	20	20	25	20	50	30	38	40	10	50	51	10	10	80
13	55	25	20	26	10	60	30	39	30	20	50	52	70	—	30

The x-ray phase analysis was performed with VRS cameras 143.25 mm in diameter with the URS-70 K1 apparatus, and with FeK radiation. The exposure was 20 hr (tube voltage 35 kv, current 10 ma).

The 52 compositions indicated in the table were chosen in the $MgO-MnO-Fe_2O_3$ concentration triangle. The diagram in Fig. 1 shows that single-phase solid solutions are formed in this system over a fairly considerable region along the line joining the ferrites of magnesium $MgFe_2O_4$ and manganese $MnFe_2O_4$. It should be noted that, in no case, was formation of hausmannite Mn_3O_4 observed; this was also confirmed by measurements of the ferromagnetic properties of the ferrites. The results were partially confirmed with the aid of the URS-50I instrument with ionization recording of the spectrum; the average detectability limit of the unconverted components (Fe_2O_3, MgO, and MnO) was 2%. At high ferric oxide contents (specimens Nos. 49, 50, 51), only Fe_2O_3 was revealed by the x-ray patterns.

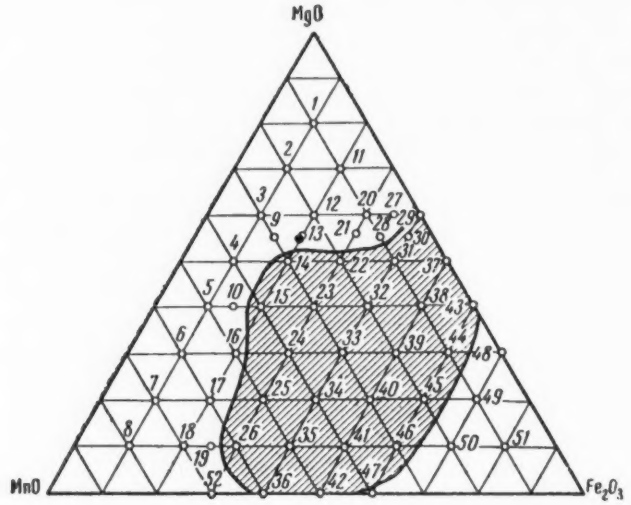

Fig. 1. The investigated ferrites and the region of solid solutions (hatched) in the system $MgO-MnO-Fe_2O_3$.

Magnesium – Chromium Ferrites

Like magnesium–manganese ferrites, magnesium–chromium ferrites were prepared by the oxide method. The starting materials were Fe_2O_3 (analytical reagent grade), Cr_2O_3 (OKh-E grade), and MgO (pure grade). The components were mixed in the required proportions, and the mixtures were heated at 1100° for partial ferritization

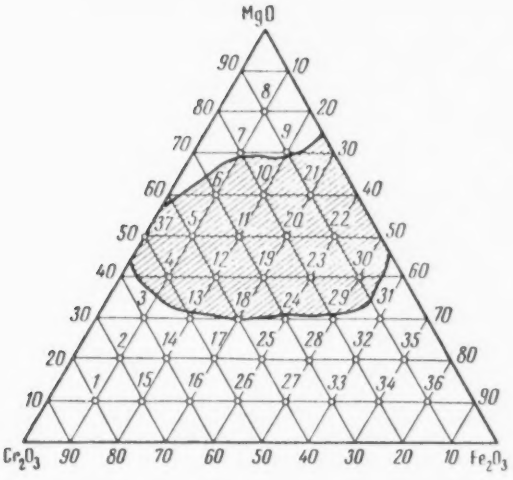

Fig. 2. Region of solid solutions (hatched) in the system $MgO-Cr_2O_3-Fe_2O_3$.

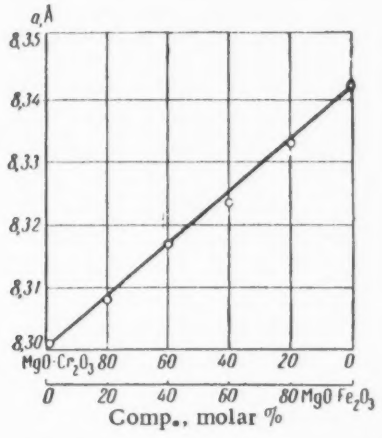

Fig. 3. Variations of the lattice constants of solid solutions of the ferrite $MgO \cdot Fe_2O_3$ and the compound $MgO \cdot Cr_2O_3$ with the composition.

and to make the particles of the mixture more active; after a second grinding, the mixture was treated with paraffin, pressed, and finally annealed in air at 1300° for 2 hr. The x-ray patterns were obtained under the same conditions as for the magnesium–manganese ferrites, but the exposure was 18 hr.

Thirty-seven compositions were chosen for investigation in the $MgO-Cr_2O_3-Fe_2O_3$ concentration triangle. The results of x-ray phase analysis are given in Fig. 2. The $MgO-Cr_2O_3-Fe_2O_3$ diagram shows that one-phase solid solutions are formed in this system in a region along the line joining $MgCr_2O_4$ and $MgFe_2O_4$. In this respect, the system $MgO-Cr_2O_3-Fe_2O_3$ differs sharply from the system $NiO-ZnO-Fe_2O_3$ investigated earlier [3], and the system $MgO-MnO-Fe_2O_3$ considered above. The difference may be explained as follows. The general formula of ferrites containing two components with bivalent ions (Mg, Zn, Ni, etc.) is of the form $(Ni, Zn)O \cdot Fe_2O_3$, i.e., only the Ni:Zn ratio varies (or, in the general case, the ratio of the bivalent ions) in the ferrite. A magnesium–chromium ferrite contains one bivalent ion and two trivalent ions: Cr^{+++} and Fe^{+++}. Therefore, the general formula of such ferrites can be written as $MgO \cdot (Cr, Fe)_2O_3$, i.e., here the Cr:Fe ratio is variable, and the region of solid solutions should lie along the line corresponding to 50% (molar) of magnesium oxide.

It should be noted that the region of solid solutions in the system $MgO-Cr_2O_3-Fe_2O_3$, shown in Fig. 2, may perhaps be somewhat smaller, because the limits of x-ray detectability of the unconverted starting materials in magnesium–chromium ferrites were not determined experimentally.

In accordance with these results, the $MgO-Cr_2O_3-Fe_2O_3$ diagram can be subdivided into five regions:

a) The line for 50% MgO. Only ferrites of the composition $Mg(Cr_xFe_{2-x})O_4$, where x varies from 0 to 2, are formed along this line. The value x = 2 (point on left) corresponds to the compound $MgCr_2O_4$ with a spinel structure. At x = 0 we have magnesium ferrite. Changes in the lattice constants of the ferrites lying on this line are shown in Fig. 3.

b) The ferrites 6, 10, and 21 – solid solutions of $Mg(Cr, Fe)_2O_4$ and MgO.

c) The ferrites 7, 8, and 9 are two-phase systems consisting of a solid solution of $Mg(Cr, Fe)_2O_4$ with MgO and excess magnesium oxide.

d) The ferrites 4, 12, 19, 23, and 30 are solid solutions of $Mg(Cr, Fe)_2O_4$ with Cr_2O_3 or Fe_2O_3.

e) All ferrites containing 30 molar % of magnesium oxide, or less, are two-phase systems. This region involved the most difficulty in x-ray phase analysis because most of the ferrites here contained unconverted iron and chromium oxides, so that reliable interpretation of the patterns was difficult. The possibility is not excluded that a nonmagnetic chromium ferrite $(Cr, Fe)_2O_3$ with a rhombohedral lattice and magnetite $FeO \cdot Fe_2O_3$ with a spinel structure are formed in this region. Work is in hand on measurements of the magnetic properties of the ferrites in this system and simultaneously more precise determination of phase composition; the results should provide a more satisfactory interpretation of the effects in the region of MgO contents below 30 molar %.

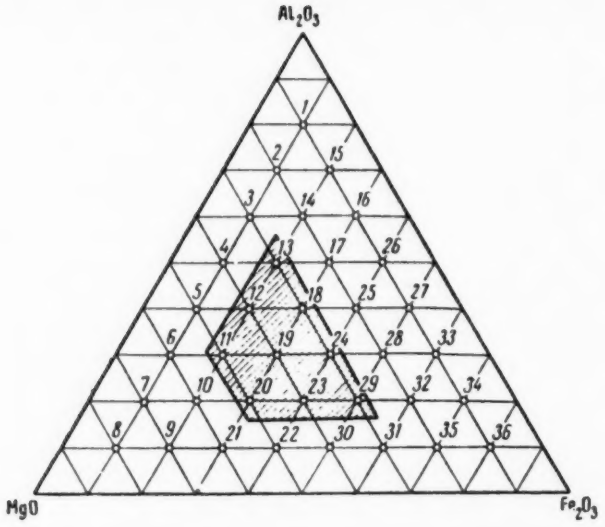

Fig. 4. The investigated compositions in the system MgO–Al_2O_3–Fe_2O_3. The hatched portion represents the region in which ferrites with the least excess contents of the components are formed.

Preliminary measurements of the magnetic properties of magnesium–chromium ferrites and of their properties in the super high-frequency range have shown that ferrites corresponding to the region of one-phase solid solutions can be used as effective phase shifters at frequencies of the order of 3000 Mc/s, i.e., they are highly effective in rotating the plane of polarization. Most magnesium–chromium ferrites have very low initial losses (one-tenth of the losses with nickel–zinc and magnesium–manganese ferrites at 3 cm wavelength; less by a factor of 1.5-2 at 10 cm wavelength), so that in these ranges they can be used in absorption systems.

Magnesium – Aluminum Ferrites

Magnesium–aluminum ferrites were prepared in the same way as ferrites of the systems MgO–MnO–Fe_2O_3 and MgO–Cr_2O_3–Fe_2O_3. The iron and magnesium oxides were of the same grades as before, and the third component was aluminum hydroxide of "pure" grade. The first heating of the mixture was at 1100° for 1 hr, and the final at 1300° for 2 hr in air. The compositions of the 36 magnesium–aluminum ferrites investigated are given in Fig. 4.

X-ray phase analysis (performed as described above) showed that one-phase solid solutions of the oxides of aluminum, magnesium, and iron were not formed in any of the specimens investigated: at high aluminum oxide contents a large excess of alumina remains in the ferrites; specimens Nos. 6, 7, 8, 9, 10, and 21 contained much free magnesium oxide; specimens Nos. 31-36 contained much free ferric oxide. In specimens Nos. 1-15 the spinel $MgAl_2O_4$ was formed, but together with the ferrite. The "purest" ferrites (i.e., ferrites with lowest admixture contents) are formed in the hatched region of Fig. 4. Thus, heating of this system in air at 1300° for 2 hr did not lead to formation of one-phase solid solutions of ferrites. This heat treatment is probably insufficient for complete formation of these ferrites. Work on this system will be continued with higher firing temperatures.

The author offers his sincere thanks to G. A. Semenov, who did all the technical part of the work, and G. I. Moshininova, for their participation in the work.

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INVESTIGATION OF THE HIGH-TEMPERATURE MODIFICATION OF BERYLLIUM OXYACETATE

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The polymorphism of beryllium oxyacetate was studied in the temperature range above the transition temperature, 145-148°, by the Debye method. The relationship was established between the monoclinic β-modification and the γ-modification, which probably has rhombic symmetry.

The high-temperature modification of beryllium oxyacetate, formed when cubic $Be_4O(CH_3COO)_6$ crystals are heated to 145-148°, has been the subject of a number of recent investigations.

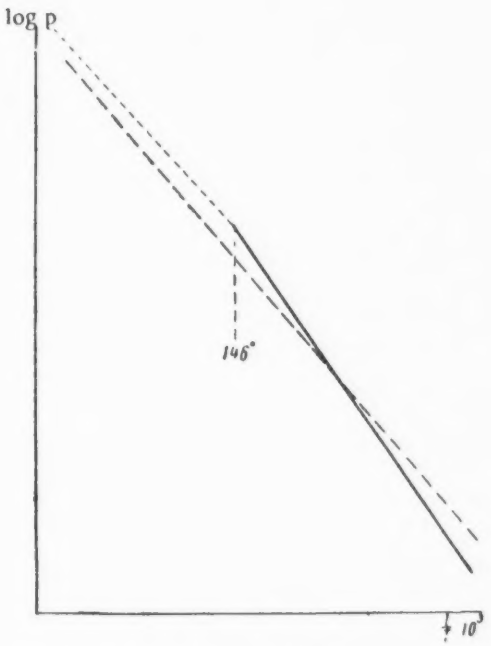


Fig. 1. Vapor pressure of beryllium oxyacetate: ——— = cubic modification; - - - - - = γ-modification; – – – – – = monoclinic modification.

Watanabe and Saito [1] refer it to the type of the so-called plastic crystals, the structure being described as rhombohedral with identity period a = 9.72 kX, α = = 54°20'. However, the authors conclude from studies of x-ray patterns obtained at 160, 170, 220, 270, and 280° that, in reality, the crystal lattice of this modification probably has a lower degree of symmetry near the transition point, and the values given for the parameters are reached only above 220°. This appears to be consistent with the fact that samples of the high-temperature modification of beryllium oxyacetate, heated above 210-220° and then cooled to room temperature, are considerably more stable and do not tend to pass immediately into the stable cubic modification [2,3].

On the basis of a study of beryllium oxyacetate, single crystals made by sublimation and formed from melts and from hot saturated $Be_4O(CH_3COO)_6$ solutions in n-butyl alcohol, and also on the basis of pycnometric determinations, the suggestion was made in 1952 [4] that the modification obtained by the above-named methods is identical with the modification formed when cubic beryllium oxyacetate is heated above 148°. However, due attention was not paid to the fact that the density of monoclinic beryllium oxyacetate samples prepared by different methods was 1.33-1.34, whereas the density of the high-temperature modification, calculated from data on volume changes during the transition at 148°, did not exceed 1.30.

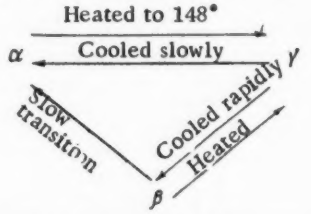
TABLE 1

X-ray Investigation of Beryllium Oxyacetate

Data of Hardt and Hendus [5]				Our data			
β-modification		γ-modification		γ'-modification		γ-modification	
I	*d*, Å	*I*	*d*, Å	*I*	*d*, Å	*I*	*d*, Å
w.*	13,41						
w.	12,13						
v.s.	8,05	v. s.	7,91	5	8,01	5	7,96
s.	7,49	v. s.	7,71	4	7,38	5	7,67
w.	7,20	s.	7,08	5	6,69	2	6,96
s.	6,71	s.	6,61	1	6,50	4	6,55
w.-m.	6,52	w.	6,07	1	5,83	1	6,04
v.w.	6,07	w.	5,80	2	5,41	1	5,77
v.w.	5,76	w.	5,44	2	4,83	2	5,39
m.	5,38	w.	5,13	2	4,58	1	5,07
m.	4,82	w.	4,90	3	4,40	1	4,83
m.	4,575	m.	4,62	3	4,16	3	4,58
m.	4,40	m.	4,31	1	4,07	3	4,29
w.-m.	4,23	m.	4,13	2	4,00	3	4,13
m.-w.	4,11	m.	3,92	3	3,83	3	3,89
w.	4,00	m.	3,75	4	3,67	3	3,73
s.	3,86	w.	3,62	2	3,46	1	3,59
v.s.	3,69			1	3,39	2	3,46
w.	3,61			1	3,34	1	3,30
				1	3,22	2	3,21
				2	3,04	2	3,10
				2	2,91	2	2,89
				2	2,78	1	2,74
				3	2,65	1	2,66
				2	2,54	1	2,59
				1	2,47	2	2,51
				1	2,43	1	2,40
				2	2,36	1	2,35
				1	2,26	1	2,30
				3	2,21	1	2,21
				1	2,13	1	2,16
				1	2,10	2	2,07
				2	2,06	1	1,98
				2	2,02	1	1,92
						1	1,88

*v.s. = very strong; s = strong; m = moderate; w = weak; v.w. = very weak. A five-point intensity scale was used.

In 1956, Hardt and Hendus [5] published a paper in which they gave ranges of interplanar spacings in crystals of the high-temperature, so-called γ-modification and of the monoclinic β-modification of beryllium oxyacetate. Without putting forward any views on the nature of the high-temperature modification, Hardt and Hendus drew attention to the negligible character of the changes in the crystal lattice in the $\beta \rightleftharpoons \gamma$ transition, and suggested the following scheme to represent the polymorphic transitions of beryllium oxyacetate:



Finally, in 1958, Semenenko and Gordeev [6] measured the vapor pressures of different beryllium oxyacetate modifications in the 117.9-177.1° range, and found that the heats of sublimation of the β- and γ-modifications of beryllium oxyacetate are very close (27.565 and 27.10 kcal/mole, respectively), and that the γ-modification is metastable over the entire temperature range in question (Fig. 1).

TABLE 2

Indexing of the X-ray Pattern of the γ-Modification [a = 9.17; b = 15.98; c = 14.44 A (± 0.05 A), density 1.30, Z = 4]

Found experimentally		Calculated		Found experimentally		Calculated	
I	*d*	*d*	*hkl*	*I*	*d*	*d*	*hkl*
5	7,96	7,99	020	3	4,58	4,58	200
		7,95	110			4,61	013and130
5	7,67	7,74	101			4,62	122
2	6,96	6,97	111	3	4,29	4,26	103
		6,99	021			4,29	032
4	6,55	6,58	012	3	4,13	4,12	023and113
1	6,04	6,03	120	3	3,89	3,88	132
1	5,77	5,67	102			3,87	202
2	5,39	5,35	112	3	3,73	3,76	212and123
		5,33	030	1	3,59	3,57	033
		5,36	022			3,61	004
1	5,07	5,00	031	2	3,46	3,48	222
1	4,83	4,81	003	1	3,30	3,29	114and024

The purpose of the present investigation was to study the polymorphism of beryllium oxyacetate above the transition temperature (145-148°) by the x-ray diffraction method. We used the Debye high-temperature method with a Unicam camera 150 mm in diameter. The temperature was measured with a platinum–platinum/rhodium thermocouple to within ± 5°. The samples for the x-ray diffraction analysis were prepared from beryllium oxyacetate recrystallized from anhydrous chloroform, of m.p. 286°. The x-ray diffraction diagrams are given in Fig. 2.

Evidently we can distinguish x-ray diagrams of three types: I, diagrams 1, 3, and 6, cubic beryllium oxyacetate; II, diagrams 2 and 4, the high-temperature γ-modification; III, diagrams 5 and 7, the γ'-modification formed on rapid or slow cooling from the γ-modification heated above 220-230°.

Results of measurements of diagrams for types II and III are given in Table 1, which also contains the ranges of interplanar spacings in crystals of the β- and γ-modifications as given by Hardt and Hendus [5]. Comparison of the data in the table shows that the γ'-modification, formed on rapid or slow cooling of beryllium oxyacetate heated above 220-230°, is identical with the monoclinic β-modification.

We attempted to interpret the x-ray diffraction pattern of the γ-modification for a rhombic lattice with identity periods a = 9.17, b = 15.98, c = 14.44 A which, for density 1.30, corresponds to four molecules of beryllium oxyacetate in the unit cell.

The indexing results are presented in Table 2. There is evidently no sense in indexing reflections corresponding to $\theta > 13$-14°, as the lattice identity periods are fairly large. Although admittedly the real lattice symmetry is not rhombic, but lower, it must nevertheless be pointed out that the agreement between the experimental and calculated values is much better for a lattice with the constants indicated above than for the rhombohedral lattice of Watanabe and Saito [1] which, for example, should not give reflections with d of 7.96 and 6.96 A.

The following conclusions concerning the nature of the γ-modification of beryllium oxyacetate can be drawn from the above data. The transition at 146-148° is indeed, as Saito and Watanabe suggested, a peculiar "prefusion" or conversion of beryllium oxyacetate into an anisotropic liquid or a "liquid" or plastic crystal. Interaction between the molecules in this "liquid" crystal is considerably weakened, and the molecules acquire greater freedom, which increases with further heating. The mutual orientation of the molecules, characteristic of cubic beryllium oxyacetate, cannot be lost immediately because of the close "intertwining" of the CH_3 groups in the crystal. It is lost gradually, as the substance is heated further, and as the temperature rises the mutual orientation of the molecules, disordered at about 200-220°, approaches continuously to the mutual orientation characteristic of the monoclinic β-modification formed by crystallization from a true melt, or on cooling of a "pseudomelt" heated above 220-230°. From this point of view, mutual orientation of beryllium oxyacetate

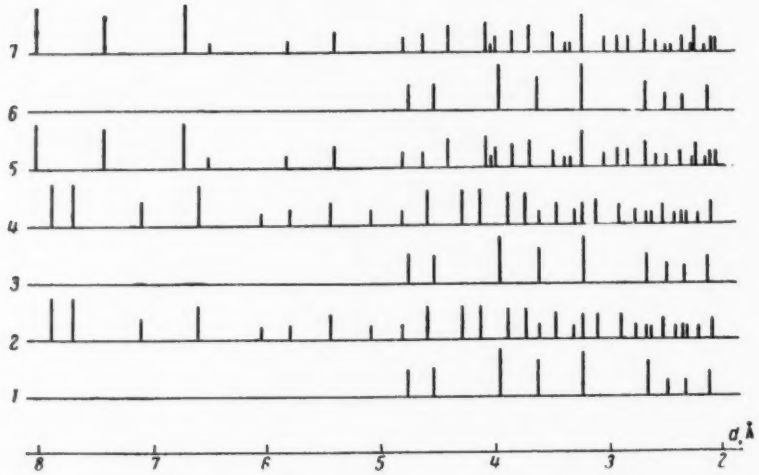


Fig. 2. X-ray diagrams of beryllium oxyacetate (the line lengths are proportional to intensities): 1) sample taken at 25°; 2) sample taken at 160°; 3) sample previously heated to 160° and taken at 25° after slow cooling (12 hr); 4) sample taken at 240°; 5) sample previously heated to 240° and taken at 25° after slow cooling (12 hr); 6) as in 3, but after rapid cooling (2-3 min); 7) as in 5, but after rapid cooling (2-3 min).

molecules in a true melt should not differ significantly from mutual orientation in a crystal heated to 270-280°; this evidently accounts for the low heat of fusion of beryllium oxyacetate, about 6.5 kcal/mole. A "pseudomelt" heated to 160-180° retains a predominant mutual molecular orientation still characteristic of the α-form, which crystallizes from it on cooling. The crystal lattice of the γ-modification or of the pseudomelt should be regarded as a somewhat "loosened" (densities 1.30 and 1.34, respectively) disordered lattice of the β-modification. It follows that the heats of sublimation of the two forms should be similar; this is found to be the case.

The above views on the transitions of beryllium oxyacetate modifications satisfactorily account for the existing experimental data and can therefore be regarded as very reliable.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ELECTRONIC STRUCTURE AND PROPERTIES OF THE NITRIDES OF REFRACTORY METALS

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It is shown that, in the general case, when transition metals with incomplete d levels combine with light nonmetals of the boron, carbon, and nitrogen type, the concentration of the bonding electrons and the nature of its distribution are determined by the number and energy state of the electrons at the d level of the metal atom and by the magnitude of the first ionization potential of the nonmetal atom.

As a particular and extreme case, the electronic structure of nitrides of transition metals is considered, together with the consequent electrical conductivity characteristics (at high and very low temperatures), homogeneity regions of the nitride phases, heats of formation, activation energy in reactive diffusion of nitrogen into transition metals, and magnetic susceptibility.

Nitrides of the transition metals exhibit simultaneously the properties of metallic compounds and ionic phases: the nitrides of titanium, zirconium, hafnium, and vanadium are predominantly metallic compounds, the nitrides of molybdenum and tungsten are predominantly ionic, while the nitrides of niobium, tantalum, and chromium exhibit joint metallic and ionic bonding, with the latter somewhat predominant.

One of the remarkable consequences of D. I. Mendeleev's periodic law is that not only is it possible to characterize systematically the physical and chemical properties of elements and their compounds, but the evolution of chemical bonding in these compounds can be traced. This has led to the discovery of a number of important crystal-chemical relationships which have formed the basis for the development of various semiconductors, magnetic alloys, and a number of other alloys of practical and theoretical importance.

The periodicity principles are applied with special success and the greatest physical clarity in investigations of the nature of alloys and compounds formed by the so-called transition metals, which have incomplete d- and f-electron levels, in addition to their usual valence electrons. We showed, in a number of earlier investigations [1-6] of various properties of compounds formed by the transition metals with each other and with nonmetals, that the character of the interatomic bonds in such compounds is determined primarily by the degree of incompleteness of the d- or f-electron levels and the ionization potentials of the metals or nonmetals.

The electronic concentration, and the position of its maximum between the metal and nonmetal atoms, vary in accordance with the number n of electrons in the incomplete d-level, the principal quantum number N of this level, characterizing its energy state, and the ionization potential I of the nonmetal.

Decrease of the criterion 1/Nn, i.e., the scattering power of the transition-metal atoms, shifts the electronic concentration maximum toward the metal atom, while an increase shifts it toward the nonmetal atom, with corresponding variations of the nature of the bond between metallic and ionic. The large number of combinations of values of 1/Nn and I gives rise to a peculiar continuous–discrete variation of bond type and of the

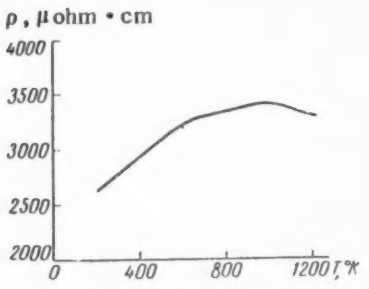

Fig. 1. Variation of the resistivity of titanium nitride with temperature.

physicochemical properties of the corresponding compounds, just as variations of nuclear charge and electron shells give rise to a continuous–discrete variation of the properties of elements in the periodic system.

The series of compounds of transition metals with nonmetals of a given period, and compounds of metals from different groups with the same nonmetal, are important for revealing these variations of bond character. The series: beryllides–borides–carbides–nitrides–oxides–fluorides of transition metals is, in particular, of interest; here statistical filling of some of the vacancies in the d-levels of the metals by the valence electrons of beryllium should be ascribed to beryllides, and transfer of some of the valence electrons of metals to the outer electron shell of fluorine should be ascribed to fluorides. These extreme cases, and more especially the intermediate stages in the series, are heterodesmic with varying proportions of what are usually termed the electronic, ionic, and other types of chemical bond. One such intermediate stage comprises the nitrides of the transition metals, which occupy a position such that, in addition to the characteristics of metallic compounds, they should exhibit certain features of ionic compounds, which are more pronounced in oxides and most pronounced in fluorides.

At normal temperatures, nitrides have higher electrical resistance than carbides [6], because of the higher ionization potential of nitrogen (14.4 ev) than that of carbon (11.24 ev) and of the corresponding displacement of the electron concentration maximum toward the nitrogen atom, i.e., because of the higher probability of electron acceptance by the incomplete d-level of the transition metal. However, this is true only for compounds of nitrogen with transition metals of low accepting power (niobium, tantalum, chromium, tungsten, molybdenum, etc.); in the light of the foregoing considerations, the nitrides of these metals should have a considerable proportion of ionic bonding. The thermal coefficient of resistance is lower for nitrides than for carbides of the corresponding metals; this indicates a relatively low bond rigidity in the nitride lattice. The resistance of nitrides increases with temperature up to 700-900°, and then decreases, as in the case of semiconductors (Fig. 1); this may be attributed either to changes in the nature of the conduction (depletion of impurity electron sources and transition to intrinsic conduction) or to structural changes (widening of forbidden zones, facilitated by low bond rigidity) [7].

TABLE 1

Activation Energies (kcal/mole) in Diffusional Formation of Certain Titanium and Zirconium Phases (first ionization potentials in ev are given in parentheses)

Metal	Diffusing element				
	Si (8,14)	B (8,28)	C (11,24)	N (14,51)	O (13,57)
Ti	5,69	9,15	17,5	33,8	24,1
Zr	—	—	17,3	39,2	23,6

Changes in the electronic concentration between the metal and nitrogen atoms with variations of the degree of incompleteness of the incomplete electron shells determine the degree of binding of the electrons and, therefore, the energy and rate of their removal from the crystal lattice. The nitrides of metals of high accepting power (titanium, zirconium, hafnium, vanadium) have an electronic structure characterized by an increased probability of the presence of the nitrogen valence electrons in the d-levels of the metal atoms; this determines a relatively high degree of electron binding in the lattice. With a decrease of the accepting power (in tantalum and niobium) the probability of electron transfer from nitrogen to the shells of the atoms of these metals decreases, and a collection of electrons donated by the nitrogen, but not accepted by the metal, arises; these electrons are adequately shielded from the fields of both nuclei and may be removed by application of an electric field, by heating, and by other forms of excitation. Therefore, the superconductivity transition temperatures of these compounds are the highest [8]; for example, the transition temperature for NbN is 15°K, for MoN 12°K, etc. The nitrides of these metals have correspondingly low work functions in thermionic emission [9].

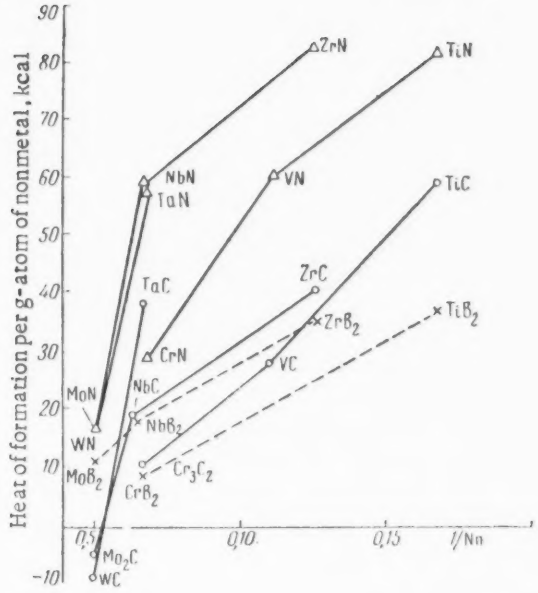

Fig. 2. Correlation between the heats of formation of borides, carbides, and nitrides, and the values of 1/Nn for transition metals.

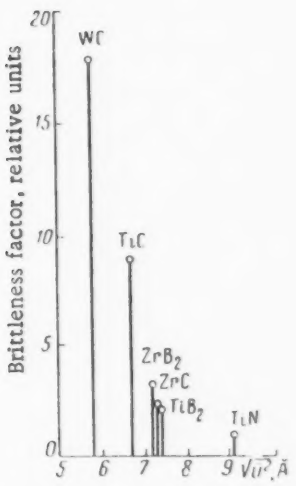

Fig. 3. Variation of brittleness factor with root mean square displacement of structural elements in the crystal lattices of metallike compounds.

This electronic state in nitrides of transition metals also gives rise to a certain freedom of variation of the metal and nitrogen atom contents, while the crystal structure is retained; the homogeneity regions of the nitrides of metals with high accepting power (titanium, zirconium, vanadium, hafnium) are fairly extensive, reaching 10-20 atomic%. Conversely, for metals of lower accepting power, these regions become very narrow, as in the case of molybdenum nitride (1-2 atomic %), owing to formation of more rigid energy states, characterized by sharply asymmetrical distribution of the electron density.

Within the homogeneity regions, the electrical resistance of nitrides falls with increase of nitrogen content owing to the increased probability of the filling of defective d-levels in the transition-metal atoms by nitrogen valence electrons; this fall of resistance increases with increasing incompleteness of the d-levels. The microhardness of the nitride phases increases with the nitrogen content.

Like all other physical and chemical properties, the heat of formation of phases such as nitrides, carbides, etc., is a function of the electron density distribution in the crystal lattice. The highest heats of formation are found for phases with the maximum asymmetry of electron density in stable states, associated either with a greater probability of filling of the d-levels of the metal atoms or with liberation of energy close to the ionization energy of the nonmetal atoms [10]. In accordance with these concepts, and with displacement of the electron density maximum toward the nitrogen atoms, nitrides have much higher heats of formation (per g-atom of nitrogen) than carbides (Fig. 2).

Determinations of activation energies in diffusional formation of nitride phases [11,12] show that they are considerably higher than the activation energies in formation of silicide, boride, and carbide phases (Table 1); this is consistent with the view that transfer of electrons is most difficult in the case of nitrogen, which has the highest ionization potential. The activation energies for formation of oxide phases are also lower than for nitrides. This agrees satisfactorily with the fact that the first ionization potential of oxygen (13.57 ev) is lower than that of carbon. From this we can, in a certain sense, ascribe a lower proportion of ionic bonding to oxides than to nitrides.

However, the magnitude of the activation energy in diffusion is merely an indication of the ease with which electrons may be transferred into the general collection of electrons, but cannot characterize the final energy state of the system. Therefore, the lower activation energy in diffusion of oxygen in comparison with nitrogen should be assessed mainly as a sign that in diffusion oxygen transfers only its first valence electron, the

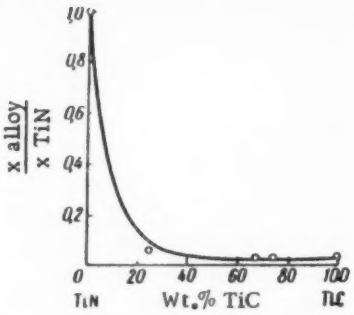

Fig. 4. Effect of composition of TiC – TiN solid solutions on their magnetic susceptibility.

TABLE 2

Asymmetry of Thermal Vibrations $\alpha(m\vartheta^2)^2 \cdot 10^a$ in the Lattices of Transition Metals, Their Carbides, and Nitrides

Metal		Carbide		Nitride	
Ti	910	TiC	5000	TiN	1700
Zr	1000	ZrC	6100	ZrN	1300
Nb	1400	NbC	6400	NbN	1700
Mo	3300	Mo_2C	2900	—	—
W	6900	WC	3500	—	—

work function of which (13.57 ev) is indeed less than the work function of the first nitrogen electron (14.51 ev). On the other hand, in the lattice of an oxide already formed, not only the first, but the second, etc., electrons are involved in bonds with transition metal atoms; the work functions of these electrons are appreciably higher in the case of oxygen atoms (second ionization potential 34.75 ev) than in the case of nitrogen atoms (29.41 ev).

Oxides therefore have a more pronounced ionic character than nitrides: they have broader forbidden zones (and, accordingly, they exhibit semiconductor properties at much lower temperatures than nitrides), higher heats of formation (owing to more asymmetric distribution of electron density), higher thermionic work functions, and narrower phase homogeneity regions (or these regions may be entirely absent).

The brittleness of nitrides, estimated by microbrittleness methods and from the root mean square displacements of the atomic complexes in the lattice [13,14] is lower than the brittleness of most of the other solid compounds (Fig. 3); this is indicative of low bond rigidity in the crystal lattices of the nitride phases, and is manifested technically in the fairly high thermal stability of nitride products.

These views on the nature of the chemical bonds in nitrides are confirmed by the investigation of asymmetry of thermal vibrations in lattices carried out by Umanskii et al. [15]. This asymmetry, represented by the product $\alpha(m\vartheta^2)^2$, where ϑ is the characteristic temperature, α is the coefficient of thermal expansion, and $\underline{m}$ is the reduced mass, is much higher for carbides than for nitrides (Table 2). For carbides of metals with high accepting power, this asymmetry approaches values characteristic of metals with a more complete d-shell; this indicates completion of the unfilled d-levels with valence electrons from the relatively easily ionized carbon atoms. The lower asymmetries of thermal vibrations for nitrides indicate a lower degree of completion of the incomplete levels by nitrogen valence electrons and a correspondingly more irregular distribution of electron density.

The results of investigations by means of x-ray spectroscopy [16,17] lead to similar conclusions concerning the nature of chemical bonding in the crystal structures of transition-metal nitrides. In particular, it was shown that the chemical bond in CrN is similar to the bond in Cr_2O_3 [16].

The magnetic susceptibility of nitrides is higher than that of carbides or borides because of the lower probability of transfer of nitrogen electrons to the d-levels of the metals and the consequent lower probability of formation of compensated spin pairs. In accordance with these views, the magnetic susceptibility decreases in formation of solid solutions of carbides in nitrides (Fig. 4) owing to displacement of the electron cloud toward the metal atom [18]. It is interesting to note that, in a number of cases, nitrides tend to give rise to metastable forms corresponding to valence formulas (for example, $TiN_{1.16}$, which is close to Ti_3N_4) [19]. Moreover, nitrogen in nitrides can be replaced by oxygen up to certain concentrations, with a corresponding intensification of the ionic characteristics of oxynitride phases [20, 21].

Thus, nitrides of the transition metals exhibit simultaneously the properties of metallic compounds and ionic phases; the relative proportions of the metallic and ionic bonding are determined by the electron deficiency of the d-level of the metal atom and the ionization potential of the nitrogen atom. In accordance with this, the nitrides of titanium, zirconium, hafnium, and vanadium exhibit mainly the characteristics of metallic compounds, while the nitrides of niobium, tantalum, and chromium reveal simultaneous metallic and ionic bonding, with the latter somewhat predominant.

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CRYSTALS OF POTASSIUM–CALCIUM, POTASSIUM–STRONTIUM, AND POTASSIUM–BARIUM OCTABORATES

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Double potassium–calcium, potassium–strontium, and potassium–barium octaborates have been prepared in the form of separate crystals. A two-circle goniometer was used for the crystal measurements. The rhombic cell constants were determined from x-ray rotation patterns. The cell constants and other crystal characteristics of the three compounds are very similar.

The octaborates of potassium–calcium $K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$, potassium–strontium $K_2O \cdot SrO \cdot 4B_2O_3 \cdot 14H_2O$, and potassium–barium $K_2O \cdot BaO \cdot 4B_2O_3 \cdot 14H_2O$ used in the investigation were prepared by the method of Gode, Keshan, and Streip [1,2,3]. Potassium tetraborate solution is added to solutions of calcium, strontium, and barium chlorides or nitrates. Bulky amorphous precipitates of variable composition are formed. In presence of a large excess of potassium tetraborate, crystals of the corresponding octaborate begin to separate out on standing, while the amorphous precipitate gradually dissolves. The crystallization rate depends on the concentration of potassium tetraborate in solution. The amorphous precipitate dissolved more rapidly near the crystals: it "thaws," like snow, around the growing crystals. This interesting effect is shown in Fig. 1. Crystallization terminates when all the precipitate has dissolved.

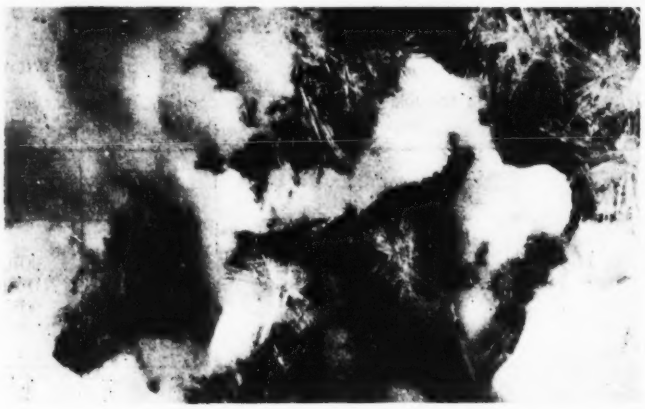

Fig. 1. Formation of $K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$ crystals from a solution containing excess $K_2B_4O_7$, in presence of an amorphous precipitate with the composition of potassium–calcium octaborate (white flakes in photograph).

TABLE 1

Results of Goniometric Measurements of $K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$ Crystals

Face symbol	Designation	φ meas	φ calc	ρ meas	ρ calc
010	*b*	0°00′	—	90°1′	90°00′
001	*c*	—	—	0°00′	0°00′
110	*m*	47°9′	47°13′	90°6′	90°00′
011	*e*	0°9′	0°00′	53°13′	53°4′
021	*g*	0°10′	0°00′	69°8′	69°24′
101	*q*	89°58′	90°00′	55°6′	55°10′
111	*a*	47°13′	—	62°57′	—

$a : b : c = 0{,}9266 : 1 : 1{,}3265$

TABLE 2

Results of Goniometric Measurements of $K_2O \cdot SrO \cdot 4B_2O_3 \cdot 14H_2O$ Crystals

Face symbol	Designation	φ meas	φ calc	ρ meas	ρ calc
010	*b*	0°00′	—	90°5′	90°00′
001	*c*	—	—	0°1′	0°00′
110	*m*	48°21′	48°18′	89°40′	90°00′
011	*e*	0°10′	0°00′	52°23′	52°08′
111	*a*	48°18′	—	62°39′	—

$a : b : c = 0{,}8902 : 1 : 1{,}2918$

TABLE 3

Results of Goniometric Measurements of $K_2O \cdot BaO \cdot 4B_2O_3 \cdot 14H_2O$ Crystals

Face symbol	Designation	φ meas	φ calc	ρ meas	ρ calc
010	*b*	0°00′	—	89°52′	90°00′
001	*c*	—	—	0°6′	0°00′
110	*m*	48°31′	48°30′	90°2′	90°00′
011	*e*	0°6′	0°00′	52°13′	52°9′
012	*f*	0°4′	0°00′	32°41′	32°46′
021	*g*	0°7′	0°00′	68°36′	68°46′
102	*n*	90°5′	90°00′	35°59′	36°2′
111		48°30′	—	62°46′	—
112	*p*	48°29′	48°30′	43°57′	44°10′

$a : b : c = 0{,}8848 : 1 : 1{,}2830$

TABLE 4

Octaborate Cell Constants

Crystals	*a*, *kX*	*b*, *kX*	*c*, *kX*	$a : b : c$
$K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$	$11{,}45 \pm 0{,}06$	$12{,}39 \pm 0{,}02$	$16{,}46 \pm 0{,}04$	$0{,}924 : 1 : 1{,}328$
$K_2O \cdot SrO \cdot 4B_2O_3 \cdot 14H_2O$	$11{,}51 \pm 0{,}02$	$12{,}89 \pm 0{,}05$	$16{,}62 \pm 0{,}07$	$0{,}893 : 1 : 1{,}289$
$K_2O \cdot BaO \cdot 4B_2O_3 \cdot 14H_2O$	$11{,}48 \pm 0{,}02$	$12{,}99 \pm 0{,}09$	$16{,}69 \pm 0{,}08$	$0{,}884 : 1 : 1{,}285$

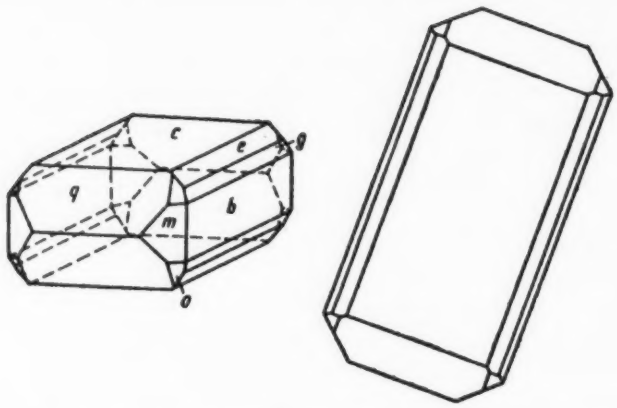

Fig. 2. Crystal of potassium–calcium octaborate.

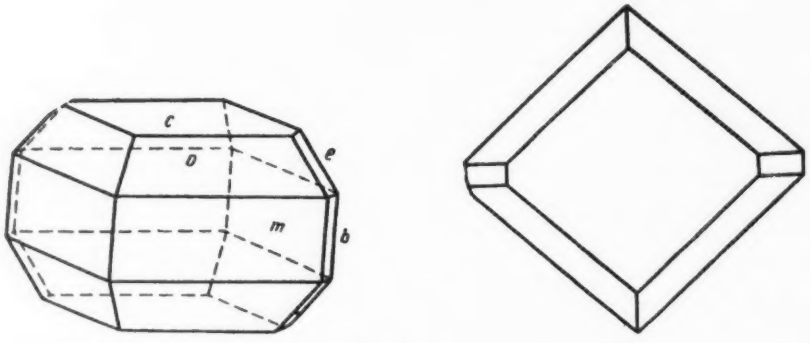

Fig. 3. Crystal of potassium–strontium octaborate.

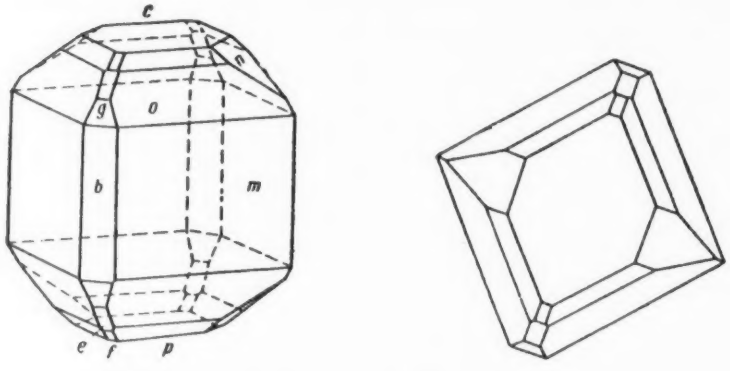

Fig. 4. Crystal of potassium–barium octaborate.

For the crystallographic measurements, especially well-grown crystals (up to 3 mm) with bright faces, were grown in a thermostat.

The experimental conditions for potassium–calcium octaborate were: 0.65 g $CaCl_2 \cdot 6H_2O$ + 4.5 g $K_2B_4O_7 \cdot 4H_2O$ in 30 ml of water, crystallization time 7 days at 28°. For preparation of potassium–strontium octaborate, 0.7 g $Sr(NO_3)_2$ + 3.5 g $K_2B_4O_7 \cdot 4H_2O$ in 50 ml of water was taken. After the solutions had been mixed, the precipitate and solution were transferred to a flask already containing small crystals of the same compound. The crystallization time was 5 days at 26°. As in the formation of potassium–strontium octaborate, the best potassium–barium octaborate crystals were obtained by addition of 0.7 g $BaCl_2$ to 4.5 g $K_2B_4O_7 \cdot 4H_2O$ in 50 ml of water, and subsequent crystallization in a thermostat at 20°.

TABLE 5

Densities of Octaborate Crystals

Crystals	d_{25}, pycn.	$d_{x\text{-ray}}$	N
$K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$	1,793	1,823	$3,93 \approx 4$
$K_2O \cdot SrO \cdot 4B_2O_3 \cdot 14H_2O$	1,936	1,950	$3,97 \approx 4$
$K_2O \cdot BaO \cdot 4B_2O_3 \cdot 14H_2O$	2,027	2,064	$3,93 \approx 4$

The crystals were filtered off by suction, washed with alcohol, and dried at room temperature. They are unstable; when left in air for several months, the crystals become turbid, and decomposition is even more rapid in the mother liquor.

The crystals of the octaborates were measured by means of a goniometer (10 crystals of each compound). Although deviations of some weak reflections were as much as ± 45', the accuracy of the average values is quite adequate because of the large number of measurements (up to 60 for bipyramid faces). The bipyramid faces of the crystals were the most perfect, so that they could be measured with high accuracy. The best reflections were obtained from potassium–calcium octaborate crystals.

According to the results of the measurements (Tables 1, 2, and 3), crystals of potassium–calcium, potassium–strontium, and potassium–barium octaborates belong to the rhombic–bipyramidal class of the rhombic system.

Crystals of potassium–calcium octaborate are shown in Fig. 2. Their form is a combination of the pinacoids b{010} and c{001}, four rhombic prisms m {110}, e {011}, g {021}, and q {101}, and a rhombic bipyramid o {111}.

The crystals of potassium–strontium octaborate have the form of thick rhombic plates (Fig. 3). They consist of a combination of two pinacoids b {010} and c {001}, two prisms m {110} and e {011}, and a bipyramid o {111}. The b and e faces are weakly developed. Some crystals had a (100) face, but only in the form of a narrow unmeasurable strip.

Potassium–barium octaborate crystals are rhombic prisms (Fig. 4). Their form is a combination of the pinacoids b{010} and c {001}, rhombic prisms m {110}, e {011}, f {012}, g {021}, and n {102}, and rhombic bipyramids o {111} and p {112}. Some crystals (about one in ten) had (121) faces. These could not be measured accurately.

The results show that the crystals of all three octaborates are similar. Thus, the spherical coordinates of the {111} face of the bipyramid (single) are very close for all three crystals, differing only by minutes. Similarity of all the other angles follows from this. The form of the crystals alters regularly in the sequence from calcium to barium: the faces of the {111} bipyramid, and especially of the 110 prism, gradually develop, while the faces of the {010} pinacoid diminish. Whereas, in the case of potassium–calcium octaborate, the {010} pinacoid, in general, determines the crystal form, it occupies a subsidiary position in the strontium compound, and is sometimes entirely absent from potassium–barium octaborate.

The unit cell constants of the octaborates of potassium–calcium, potassium–strontium, and potassium–barium were determined (Table 4) by the rotation method with effective film diameter taken into account (the asymmetric method); CuK radiation, exposure 7-10 hr.

Comparison of the results reveals a close similarity of the lattice constants for all three compounds, with a regular increase (with the exception of a) in the sequence from calcium to barium.

According to the literature, the densities are: potassium–calcium octaborate $d_{25} = 1.80$ [1]; potassium–barium octaborate $d_{25} = 2.04$ [3]. We used our specimens for more accurate determinations (pycnometrically in bromobenzene) of the densities of the crystals of all three octaborates. The number N of the formula units in the unit cell was found from the cell constants and densities (Table 5).

The results indicate that transition from calcium to barium in the double octaborates have little effect on the crystal characteristics. It is to be expected that the crystals would have similar structures.

SUMMARY

The preparation of crystals of double borates of calcium, strontium, and barium of the type $K_2O \cdot MeO \cdot 4B_2O_3 \cdot aq$ is described. Crystals of potassium–calcium, potassium–strontium, and potassium–barium octaborates are isomorphous and belong to the rhombic–bipyramidal class of the rhombic system. The simple crystal forms, cell constants, and densities of the three octaborates were determined.

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INTERACTION OF GALLIUM, INDIUM, THALLIUM, GERMANIUM, TIN, AND LEAD WITH BORON

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The results of an investigation of the interaction of gallium, indium, thallium, germanium, tin, and lead with boron are given. These results show that it is impossible to obtain the borides of these elements or of solid solutions of boron in them.

The absence of any interaction between elements of IIIB and IVB subgroups and boron is attributed to the completeness of the inner electron shells and the high second ionization potentials of these elements.

It has now been established that all alkaline-earth metals and the transition-group metals, including the lanthanide and actinide series, form compounds with boron. As yet no individual borides of the alkali metals, and of other metals with completely filled internal electron shells, found in the B-subgroups of the periodic system, have been reported. In particular, there are no reports of the borides of gallium, indium, thallium, germanium, tin, and lead.

The predominant formation of boride phases by metals of the transition groups can be attributed to donor–acceptor interaction between atoms of the transition metals, with incomplete internal d- and f-electron shells, and the easily ionized boron atom, which contributes three electrons to the bond, including the first p-electron with special ease. Phases of the metallic type are formed with a common electron gas between the metal and boron atoms, and with a distribution of electron concentration leading to a certain proportion of covalent or ionic bonding.

If the possibility of formation of borides of B-subgroup metals with complete internal electron shells is considered from this viewpoint, it appears that such formation is improbable, especially in view of the very high ionization potentials of many of these metals (Table 1).

In estimating the possible formation of borides by metals of IIIB subgroup, it should be noted that, in the case of indium, there is some likelihood of the formation of a common electron gas with boron because, apart from the fact that it has the lowest first and second ionization potentials, the indium atom has an incomplete 4f-shell which, under certain conditions, can act as an electron acceptor, as was found to be the case in alkaline-earth metals [1].

Hardly anything is known from the literature about the interaction of gallium, indium, and thallium with boron, apart from the experiments of Giebelhausen [2], who introduced amorphous boron into molten thallium and kept the melt in a magnesite tube at 1500-1600° in a current of hydrogen. He did not detect any interaction; this result confirms qualitatively the view put forward above concerning the low probability of thallium–boron interaction.

TABLE 1

Electronic Structures of the Atoms of Gallium, Indium, Thallium, Silicon, Germanium, Tin, and Lead

Metal	Incomplete level	Valence electrons	Ionization potentials, ev		Metal	Incomplete level	Valence electrons	Ionization potentials, ev	
			I	II				I	II
Gallium	—	$4s^2\ 4p^1$	5,97	20,39	Silicon	—	$3s^2\ 3p^2$	8,14	16,29
Indium	$4f$	$5s^2\ 5p^1$	5,76	18,76	Germanium	—	$4s^2\ 4p^2$	8,10	15,95
Thallium	$5f$	$6s^2\ 6p^1$	6,08	20,29	Tin	$4f$	$5s^2\ 5p^2$	7,54	14,56
					Lead	$5f$	$6s^2\ 6p^2$	7,37	14,91

TABLE 2

Results and Conditions of Experiments on the Interaction of Gallium, Indium, and Thallium with Boron

Expt. No.	Charge	Medium	Temp. of expt., °C	Time, min.	Results
I	$Ga_2O_3 + 7B$	Vacuum	1500	35	Reduction of oxide to metal, condensing on cool parts of furnace
II	$Ga_2O_3 + B_4C + 2C$	The same	1600	30	The same
III	$Ga_2O_3 + 2B_2O_3 + 9C$	The same	1500	30	The same
IV	$Ga_2O_3 + 4B$	Hydrogen	800	30	Formation of a sinter of boron with dissemination gallium particles
			900	30	The same
V	$Ga_2O_3 + 8B$	The same	900	30	The same
VI	$Ga_2O_3 + 12B$	The same	900	30	The same
VII	$Ga_2O_3 + 24B$	The same	900	30	The same
VIII	Ga + B	Argon	1000	50 hr	No interaction; after contact with boron, the gallium solidifies between 0 and 5*
IX	Ga + B	Vacuum*	1200	240	The same
X	$In_2O_3 + 15B$	The same	1650	60	Reduction of oxide to metal, condensing on cool parts of furnace
XI	$In_2O_3 + B_4C + C$	The same	1000	60	The same
XII	$In_2O_3 + 4B$	Hydrogen	800	15	The same
XIII	In + B	Vacuum*	1200	240	The same
XIV	$Tl_2O_3 + 7B$	The same	1200	10	Reduction of Tl_2O_3 to Tl_2O; no interaction between thallium and boron
XV	$Tl_2O_3 + 4B$	Hydrogen	400	30	The same
			550	30	The same
			650	30	The same
XVI	Tl + B	Vacuum*	1200	240	No interaction detected

*In evacuated quartz bulbs.

The object of the present investigation was an experimental study of the interaction of gallium, indium, and thallium with boron. The following methods were used: 1) reduction of the oxides with boron in a vacuum; 2) reduction of mixtures of the oxides and boron with hydrogen; 3) reduction of mixtures of metal oxides and boric anhydride with carbon; 4) reduction of oxides with boron carbide; 5) direct combination of the metals with boron.

The starting materials were the pure oxides of gallium, indium, and thallium, and the metals themselves. The boron used in the work was 99% pure; the boron carbide was the purified technical product containing traces of iron, silicon, and magnesium.

The charge compositions used in these methods are given in Table 2, which also gives the experimental conditions and the results of qualitative study of the products.

Gallium – Boron

A series of experiments on the interaction of gallium with boron was performed under vacuum; it was assumed that, despite the fairly high vapor pressure of gallium at high temperatures, if it formed compounds with boron the rate of combination should prevail over the evaporation rate; incidentally, this would indicate high chemical stability of the compounds. However, the results of these experiments (I, II, III) showed that under these conditions gallium oxide is reduced to the metal, which is deposited on the cooled parts of the furnace. Interaction of gallium oxide with boron in a hydrogen atmosphere (Expt. IV) yields sinters consisting of boron with disseminated particles of gallium; the degree of reduction of gallium oxide to the metal reaches 98-99%. Similar results were obtained when a very large excess of boron was used (Expts. V-VII). When gallium covered with boron was heated in argon for 50 hr at 1000° (Expt. VIII) or in a sealed quartz bulb for 4 hr at 1200° (Expt. IX), an alloy is formed which solidifies at a much lower temperature than pure gallium (between 0 and −5°, as compared with 29.8° for gallium). However, the solidified "alloy" melts again at a temperature approximately equal to the melting point of pure gallium. Therefore, either boron is soluble in liquid gallium but not in the solid metal, or (which is more probable) it causes a sharp lowering of the surface tension of gallium itself, giving rise to a metastable state which is eliminated immediately after removal of the surface film. Comparison of the x-ray diffraction patterns of pure gallium and gallium solidified at −5° showed them to be identical, with the same lattice constants: a = 4.51, b = 7.61, c = 4.48 kX.

Indium – Boron

None of the experiments on interaction of indium or indium oxide with boron, or boron-containing materials, revealed any sign of compound formation or of solubility (Table 2, Expts. X-XIII). Rapid reduction of indium oxide with volatilization of the metal begins at much lower temperatures than in the case of gallium.

Thallium – Boron

In an attempt to reduce thallium oxide with boron under vacuum (Table 2, Expt. XIV) at 1200°, a brown substance, consisting mainly of thallous oxide Tl_2O, volatilized and condensed on the cold parts of the furnace. None of the other experiments (XV, XVI) gave an indication of the formation of solutions or compounds of thallium with boron.

The results therefore show that boron does not interact to any extent with gallium, indium, or thallium; this is consistent with the views based on a consideration of the electronic structure of the atoms of these metals and boron.

The easy reducibility of gallium and indium oxides by boron under vacuum, without any interaction between the metals and boron, can be utilized in preparation of very pure gallium and indium by reduction of the oxides with boron and simultaneous sublimation.

Germanium – Boron, Tin – Boron, Lead – Boron

Consideration of the interaction of boron with the elements of the IVB subgroup of the periodic system (carbon, silicon, germanium, tin, and lead) shows that, whereas compounds of boron with carbon are known and there are some data on boron–silicon compounds, there is no information at all on compounds of boron with germanium, tin, or lead.

Boron and carbon form the chemically stable compounds $B_{12}C_3(B_4C)$ and $B_{13}C_2$ [3,4], characterized by pure covalent bonding. Moissan [5] reported that boron forms two compounds with silicon; the formulas B_3Si and B_6Si ascribed to these compounds were confirmed by later investigations [6,7]. The compound B_6Si was investigated by means of x-ray diffraction [7], when the crystal-chemical causes of the difficulty of its formation were elucidated. When B_6Si and other boron–silicon compounds are formed, B–Si bonds of a metallic type which is due to the higher metallic character of silicon as compared with boron are formed, in addition to covalent Si–Si and B–B bonds. When metallic bonds appear, the rule established in [8] for formation of hexa- and tetraborides begins to operate. This rule is that five electrons are required for the formation of spatial groupings of boron atoms, i.e., for the formation of, say, a hexaboride, the metal atom must transfer to the boron atom two external electrons for creation of five hybrid orbits formed from s-, p-, and excited d-functions. Such transfer

is possible because of the not very strong binding of these electrons by the atom; in particular, it was shown that the first ionization potential must not exceed 6.6-6.8 ev, and the second 11.5-12 ev.

In the case of silicon, both the first and the second ionization potentials are above these limits (Table 1), but the hexaboride structure is formed mainly by means of the as yet stable covalent bonds although, as was noted, the formation proceeds with considerable difficulty.

From this it is to be expected that, in the further sequence from silicon to germanium, tin, and lead, i.e., with further increase of metallic character and loss of covalent bonds, the possibility of formation of hexaborides or other boron compounds almost vanishes because the specified conditions [8] are not fulfilled. To verify this view, attempts were made to obtain borides of germanium, tin, and lead by various methods; in particular, the experimental possibilities of germanium hexaboride formation were studied in detail.* Pure, thoroughly calcined germanium oxide (99.9% GeO_2), boron carbide B_4C, pure germanium made from powdered single crystals, and lamp black containing 99.98% C were used for the experiments. The reaction products were analyzed chemically and studied by the x-ray powder method in a camera 114.6 mm in diameter with CuK_α radiation and a nickel filter.

In the first series of experiments, germanium dioxide was subjected to vacuum-thermal reduction with a mixture of boron carbide and lamp black in attempts to obtain germanium hexaboride by the reaction

$$2GeO_2 + 3B_4C + C = 2GeB_6 + 4CO$$

at temperatures between 1000 and 1400° with 1 hr of exposure at each temperature. Variations of the rate of pressure drop in the furnace and of the briquet weight with heating time and temperature were studied, and the products were analyzed chemically and by the x-ray phase method. The carbon monoxide pressure in the furnace fell continuously at 1000 and 1100° during 1 hr exposures, while at 1200° it reached a certain constant value after 45 min. At this temperature, the yield by weight, calculated for the reaction proceeding to GeB_6 formation, was about 100%; beyond this, the yield fell sharply to 90% at 1300°, while at 1400° almost the entire reaction mass volatilized under vacuum. Chemical analysis showed that at 1200° the sum of the germanium, boron, and carbon contents in the reaction product was about 80%; this means that, first, reduction of GeO_2 is incomplete; and, second, that it does not lead to hexaboride formation. At 1300° the total Ge + B + C content was 98-99%, but the carbon content of the reaction product was 12-13%, with 39-40% Ge and 45-46% B. All the carbon in the product was free, not combined either with boron or with germanium. The x-ray pattern of the product formed at 1200° showed that the principal phase was germanium with admixtures of B_4C + GeO_2. This reaction therefore results in the formation of germanium, which volatilizes under vacuum at high temperatures, together with the boron, which is formed simultaneously.

Reduction of germanium dioxide with boron for the reaction

$$GeO_2 + 3B = GeB_6 + 2BO$$

gave, on the whole, similar results: a mixture of germanium and boron was formed.

In the next series of experiments, mixtures of germanium and boron (designed to give GeB_6) were heated in argon at 800° for 2, 4, and 8 hr; at 900° with the same exposure times, and at 1200° for 1.5 hr; in addition, mixtures of germanium and boron powders were sintered by hot pressing in a graphite mold at 2000° for 5-10 min. In all experiments on sintering of germanium–boron mixtures in argon, x-ray phase analysis showed that the principal phase in the reaction products is germanium with an admixture of boron, while in hot pressing the main phase is germanium with an admixture of boron carbide formed by reaction of boron from the charge with the graphite of the mold.

Calculation of the lattice constant of germanium from the x-ray patterns of the products formed both from germanium dioxide and from germanium gave the value a = 5.65 A, which is in good agreement with the literature value for pure germanium [9]. In addition to showing the absence of germanium–boron compounds, this result indicates that boron is insoluble, or very slightly soluble, in germanium, as within the limits of experimental error the lattice constant of germanium obtained after contact with boron under the most diverse temperature conditions retains the same value.

*V. P. Dzeganovskii and L. M. Khrenova took part in the experimental work.

Microhardness determinations performed with germanium obtained from a number of experiments, including the hot pressing of germanium–boron mixture, gave the value 860 kg/mm^2, which coincides exactly with the value found in [10] for very pure germanium. Incidentally, this indicates that not only boron, but also carbon is insoluble in germanium, as carbon and germanium were in contact at high temperatures in a number of experiments. The hardness of boron remains unchanged after contact with germanium; this shows that germanium is insoluble in boron.

Similar results were obtained in attempts to prepare tin and lead borides.

SUMMARY

Investigations of the interaction of boron with gallium, indium, thallium, germanium, tin, and lead with boron showed that these elements do not form chemical compounds or solid solutions with boron.

The absence of any interaction between these elements and boron is explained in the light of a discussion of the electronic structure and energy characteristics of the valence electrons of metals of the IIIB and IVB subgroups of the periodic system.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

REVIEWS

APPLICATIONS OF NUCLEAR QUADRUPOLE RESONANCE IN CRYSTAL-CHEMICAL INVESTIGATIONS

II. METHODS AND RESULTS OF EXPERIMENTAL INVESTIGATIONS *

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A brief description of quadrupole radiospectrometers is given. The main trends in work on nuclear quadrupole resonance (NQR) are defined: attempts to investigate electron density distributions in molecules; searches for empirical relationships between chemical properties and NQR frequencies; applications of NQR to certain problems of the structure of real crystals. Data on the NQR spectra of 477 different chemical compounds have been collected for the first time.

1. Frequency Ranges

The frequency at which quadrupole resonance occurs depends (see Part I of this review) on the absolute values of the quadrupole moment Q of the nucleus, the gradient $\underline{q}$ of the electric field created in the center of the nucleus by all the neighboring charges, and on the spin function $f(I)$. The table of the quadrupole moments of the stable isotopes, given in Part I, clearly shows that values of Q vary periodically with increase of mass number. The "normal" tendency is an increase of Q down each group of the periodic system. Exceptions to this tendency are Cs^{133} in group I, and Bi^{209} in group V.

The value of $\underline{q}$ is determined by many factors, and may vary severalfold for a given atom in accordance with the state of the chemical bond.

The nuclear spin I also varies from nucleus to nucleus, resulting in appreciable variations of $f(I)$.

The consequence of the combined influence of these three factors is that, for example, chlorine exhibits NQR in the range from 5 to 70 Mc/sec, and bromine, in the range from 40 to 270 Mc/sec.

Figure 1 shows the frequency ranges in which transitions between quadrupole energy levels of various elements in different chemical compounds have been observed. It can be seen that a quadrupole radiospectrometer intended for observation of the resonance of all isotopes suitable for the purpose should cover a very wide range of frequencies, from the long-wave radio-frequency range to decimeter waves.

2. Apparatus for Observation of NQR

It should be emphasized that continuous searching for an unknown weak signal in a wide frequency range is an extremely difficult problem which cannot as yet be regarded as finally solved. The apparatus described below was used by most workers, not because entirely satisfactory solutions to the problem had been found, but owing to absence of better equipment.

*For Part I of this review, see Zhurnal Strukturnoi Khimii 1, 2, 252 (1960).

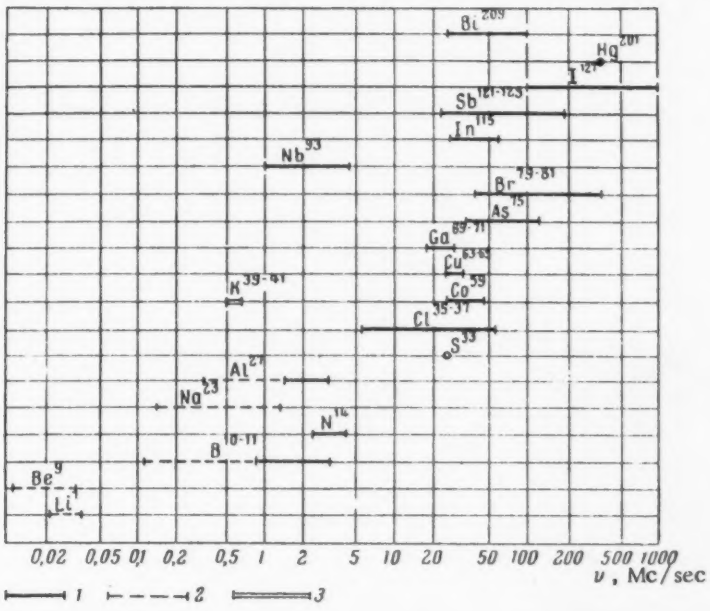


Fig. 1. Chemical shifts of NQR frequencies for different elements, measured: 1) by means of NQR; 2) from splitting of magnetic resonance lines; 3) by the pulse technique.

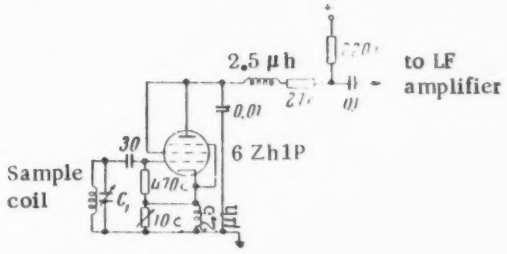


Fig. 2. The Hopkins autodyne circuit.

The techniques are based on the use of slightly modified autodyne circuits of the type developed for observations of nuclear magnetic resonance [1]. In most NQR spectrometers, the signal is produced by a regenerative or superregenerative oscillating detector. The processes in the regenerative oscillating detector may be briefly described as follows.

The substance to be investigated is placed in the coil of the oscillator circuit (Fig. 2). Oscillations, the frequency of which can be varied smoothly (for example, by means of a variable capacitor), are induced in the circuit by suitable selection of feedback. When the frequency ν of the oscillations in the circuit satisfies the condition $h\nu = \Delta E$, where ΔE is the distance between the quadrupole levels, the substance in the coil begins to absorb energy from the resonant circuit, varying the active conductance component of the latter. Whereas, before resonance, the conductance of the circuit is G, at the instant of resonance it is $(1 + \gamma)G$. Calculations show that changes in the conductance of the circuit result in changes of the high-frequency amplitude; an amplitude of U_0 before resonance becomes $(1 + \epsilon)U_0$ at resonance. The modulation of the circuit conductance γ is proportional to the imaginary component χ'' of the magnetic susceptibility of the specimen, the filling factor η, and, with certain assumptions [1], the figure of merit of the circuit Q_0:

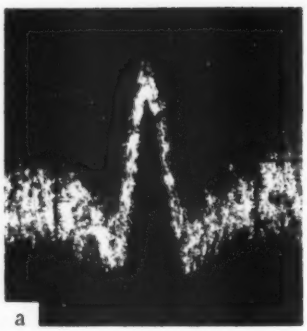
$$\gamma = 4\pi\eta\chi''Q_0. \qquad (1)$$

The filling factor η is the ratio of the high-frequency energy in the specimen to the total energy of the circuit.

The imaginary component of magnetic susceptibility [2] is determined by the properties of the specimen

$$\chi'' = f(I)\cdot\frac{N_0\mu^2}{kT}\cdot\frac{\nu}{\Delta\nu}, \qquad (2)$$

where N_0 is the number of resonating nuclei in 1 cm^3; μ is their magnetic moment; ν is the frequency of the NQR line; $\Delta\nu$ is its half-width. The spin function $f(I) \sim 1$. It follows from Eqs. (1) and (2) that, for the strongest



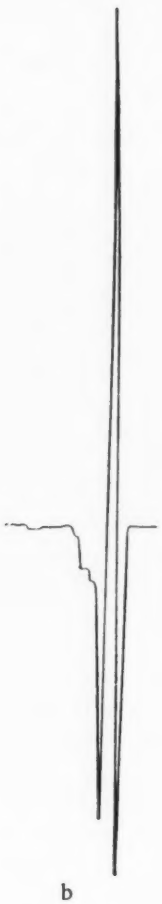


Fig. 3. a) NQR signal from 20 cm^3 of sodium chlorate, observed by means of a regenerator and broad-band amplifier; b) same signal after synchronous detection at $2\nu_m$ frequency.

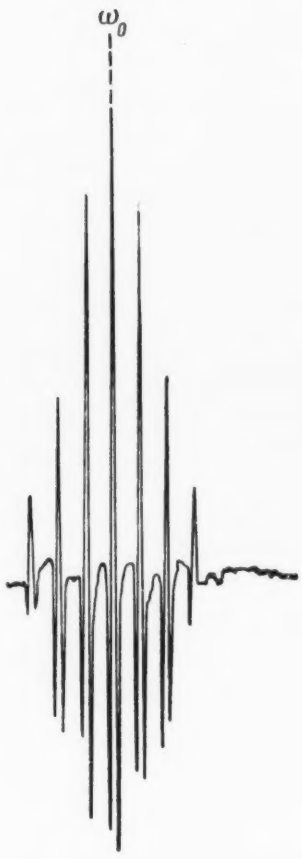


Fig. 4. Grequency trace in superregenerator.

NQR signals at $Q_0 \sim 10^2$, the conductance modulation has a very low value: $\gamma \lesssim 10^{-4}$. Spectrometer design calculations must be based on values of γ of the order of 10^{-6} to 10^{-7}.

The question of the relative change ϵ of the circuit voltage at a given γ was considered by Shpigel' et al. [3], and by Buyle-Bodin [4]. In [3], the transition of the oscillator from one steady state to another on introduction of additional quenching into the circuit is considered. It was shown that the change of the circuit voltage is directly proportional to γ and inversely proportional to the voltage before introduction of the additional quenching. The relationship $\epsilon \sim \gamma U_0^{-1}$ prevents the use of high radio-frequency voltages in the circuit, and usually $U_0 \leq 1$ v in NQR observations with the aid of regenerative spectrometers. Approximate calculations based on the data in [3] show that for the usual NQR signals, $\epsilon \sim 10\gamma \sim (10^{-5}\text{-}10^{-6})$. In these calculations, only the operation of the autodyne as an oscillator was taken into account, and detection conditions were not considered. Buyle-Bodin's investigation was concerned with detection in the regenerative oscillating detector: the ϵ/γ ratio and the signal form were shown to depend on the time constant of the detecting circuit. It follows from calculations and from Buyle-Bodin's experiments that at maximum sensitivity, which is the spontaneous goal of nearly all workers in spectrometer tuning, the signal reproduced by the detector is very far from the true form of the NQR absorption line. Examniation of theoretical work and experimental results leads to the conclusion that the possibilities of raising the sensitivity of regenerative oscillating detectors are almost exhausted. Many regenerative NQR spectrometers are described in the literature. They are all either different versions of the Hopkins circuit [5-9], or modifications of the Pound circuit [1,10-15], and are all of much the same sensitivity. The Pound

circuit is preferable, because it embodies a successful solution of the problem of stabilization of the generator and detector with large frequency changes.

Wang's attempt [8] to raise the sensitivity of the Hopkins circuit by introduction of feedback from the detected NQR signal led to an interesting version of the regenerator. However, G. K. Semin's measurements showed that, in the cases when Wang's circuit gives a real sensitivity increase, it introduces considerable distortion into the signal form.

Very small voltage changes in the circuit are detected by the modulation method: the frequency ν_0 is swung over a narrow range in accordance with the equation $\nu = \nu_0 + \Delta\nu_m \sin 2\pi\nu_m t$. The frequency deviation amplitude $\Delta\nu_m$ chosen is approximately 5-10 times the width of the NQR line; the deviation frequency is chosen in the 20-300 cps range. Sometimes magnetic modulation is used instead of frequency modulation: a magnetic field sufficient for complete blurring of the signal is applied at frequency ν_m to the coil (see Part I, Section 2). In either case, if $\nu_0 = \nu_{res}$, the voltage at the generator-tube grid is modulated by the audio frequency ν_m with a modulation amplitude equal to the signal amplitude ϵU_0. As the grid current–grid voltage relationship is nonlinear, the tube detects this voltage and pulsation at frequency ν_m appears in the anode current. This pulse potential is fed to a low-frequency amplifier (LFA) with a transmission band of the order of 1-5 kc/sec, sufficient to let through, without serious distortion, the harmonics necessary for reproduction of the signal form.

The amplified signal voltage is fed to the vertical plates of an electronic oscillograph, the scanning of which is synchronized by the modulating voltage. A signal similar to that shown in Fig. 3a then appears on the screen. It can be seen that with this "wide-band" method of observation the signal is comparable with fluctuation noise of the generator-detector.

A fairly obvious way of raising the signal-to-noise ratio is by increasing the amount of substance taken for the investigation. In view of the weakness of the NQR signals, it is important that the specimen should occupy a volume in which most of the energy of the radio-frequency magnetic field is concentrated, i.e., such that $\eta = 1$. Livingston [6] proposed the use of metallic containers for the sample coils for this purpose. Usually, with a coil about 1.5-5 cm^3 in volume, from 20 to 70 cm^3 of a polycrystalline specimen is placed in the container. Naturally, different regions of the specimen in the container are connected in different ways with the coil and make unequal contributions to the observed signal. E. I. Fedin's measurements of field strength in a container showed that with this technique a tenfold increase of specimen volume gives roughly a twofold increase of signal-to-noise ratio.

Unfortunately, such large amounts of substance are not usually available. It is then necessary to decrease η and to use ampoules inserted into the coil. The usual volume of our ampoules is 0.5-2 cm^3. The use of ampoules has one important advantage: if necessary, the specimen can be sealed, and after determination of the quadrupole spectrum it can be recovered without any damage for further investigation. However, with ampoules of this size, the NQR spectra of very many compounds cannot be seen on the oscilloscope screen with broad-band amplification. Thus, the sensitivity of regenerative quadrupole spectrometers very often proves inadequate. Therefore, superregenerative oscillating detectors, giving five- to tenfold sensitivity gains, are widely used in work on nuclear quadrupole resonance. In a superregenerator the radiofrequency oscillations are not continuous, but are "quenched" at a quenching frequency ν_q satisfying the condition $\nu_m \ll \nu_q \ll \nu_0$. The sensitivity gain is achieved by formation of the signal under nonsteady generation conditions and by the effective use of very high radiofrequency voltages (up to 40 v) in the circuit. A characteristic feature of the superregenerator is the multicomponent character of its resonance curve: in addition to oscillations at the circuit tuning frequency ν_0, oscillations of frequencies $\nu_0 \pm n\nu_q$, where $n = 1, 2, 3, \ldots$ exist in the circuit. Therefore, in passing through a single quadrupole resonance line, the superregenerative spectrometer records $2n + 1$ NQR "signals," of which the central one is the true signal, and the others are superregenerative side-band responses. This multiplication of the signals often hinders accurate measurements of NQR frequencies and analysis of NQR multiplet spectra. However, this same property of the superregenerator often proves useful for identification of weak NQR signals which may be confused with accidental distortion of the zero line. The reason is that, first, the superregenerative side-band responses of the quadrupole signal vary regularly in amplitude and are separated by equal frequency intervals; and second, that they alternate in phase. Figure 4 shows the result of a measurement of the frequency of a superregenerative oscillating detector. The oscillating detector operated as a highly sensitive radio receiver, receiving on a small antenna the almost monochromatic signal emitted by a standard-signal oscillator. As a result, a multicomponent frequency trace was recorded with slow variation of the frequency ν_0 of the oscillating

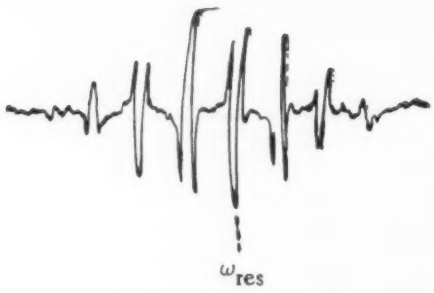


Fig. 5. NQR signal of the rare isotope Cl^{37} from 1 g of p-dichlorobenzene, obtained with a superregenerative spectrometer.

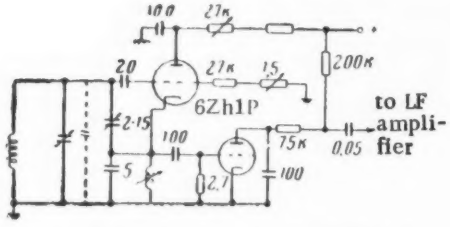


Fig. 6. Superregenerative oscillating detector for the chlorine band.

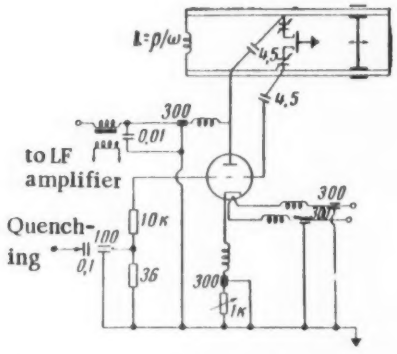


Fig. 7. Superregenerative oscillating detector for the bromine band.

detector. It can be seen that the peaks of the superregenerative spectrum of this trace are all of the same polarity. Figure 5 shows a trace of an NQR line. Here, alternating polarity of the superregenerative components of the signal is clearly seen.

Our measurements suggest that the superregenerative oscillating detector reacts to a greater extent to radiation of energy from a nuclear spin system than to the corresponding absorption of energy.

Dean and Pollak [16] described an ingenious method for eliminating the superregenerative side-band response of the signal by slow modulation of the quenching frequency ν_q. Variations of ν_q cause the components to shift to the right and left of the undisplaced position, so that in synchronous detection (see below) these components cannot accumulate in the RC circuit and become "blurred." The circuit tuning frequency ν_0 does not depend on ν_q, and the true NQR signal is recorded almost without loss of intensity.

The physical processes taking place during formation of the NQR signal in the superregenerator are very complex. It can be regarded as experimentally proven that, because of this, the true form of the quadrupole resonance line undergoes considerable distortion in observations with the superregenerative spectrometer [17]. This has to be accepted in cases where high sensitivity is required and precise measurement of the NQR line widths is not needed.

Our superregenerative oscillating detector circuits are shown in Figs. 6 and 7. The oscillating detector for the chlorine band (Fig. 6) has a circuit with concentrated constants. It is assembled in accordance with Dean's circuit [18], with the difference that a separate tube is used for detection of the NQR signal. This is to ensure reliable operation of the detector during changes of the generator operating conditions in searches for unknown resonance frequencies. A similar device was used independently by Safin [19], and also by Buyle-Bodin [4] with a regenerator.

At frequencies from 100 to 350 Mc/sec, satisfactory results were obtained with the two-wire circuit shown in Fig. 1. Push-pull oscillators give good results in this band [20-23]. Oscillators with coaxial resonators are used at higher frequencies [24].

Unfortunately, in most cases the sensitivity of the superregenerative spectrometer is still inadequate in wide-band signal observations.

For further increase of the spectrometer sensitivity, the transmission band of the amplifier must be narrowed sharply, as for a band width of $\Delta\nu$ the noise voltage at the amplifier output is proportional to $\sqrt{\Delta\nu}$ [1]. The synchronous detector [25] provides an effective means for narrowing the transmission band. If the synchronous detector is followed by an RC circuit with a time constant of 10 sec, the detector transmission band is equal to 0.1 cps. This means that, in comparison with broad-band observation of the signal, when $\Delta\nu \geq 500$ cps, the sensitivity can be raised 100-fold and more by synchronous detection, owing to narrowing of the transmission band. This is attained at the cost of a corresponding increase in the time required for the experiment. The signal from the synchronous detector is usually fed to a direct-current recording millivoltmeter. A typical trace of an NQR signal demonstrating the sensitivity gain achieved in this way is shown in Fig. 3b. The characteristic

form of the signal on the trace is explained by the fact that the synchronous detector was tuned to the second harmonic of the modulation frequency. It is then possible to avoid the influence of parasitic amplitude modulation [26], which is a serious obstacle in NQR observations with a frequency-modulated regenerative spectrometer. Recording of the second harmonic of the signal was proposed by Livingston and examined in detail by Fedin and Konstantinov [26]. The need to tune the synchronous detector to $2\nu_m$ frequency is completely eliminated with magnetic modulation of the signal, and in some instances also with frequency modulation of superregenerative oscillating detectors, which are less liable to parasitic amplitude modulation than regenerators.

Examination of the signal in Fig. 3b may give a somewhat exaggerated idea of the sensitivity of modern quadrupole radiospectrometers. In reality, it is exceptionally difficult to detect a signal $^1/_{100}$ as strong as that shown in Fig. 3b if the frequency of this weak signal is not known. The reason is that, in prolonged frequency searching, the tuning of the oscillating detector is disturbed and zero stability is lost. It is not much easier to raise the zero stability than to improve the sensitivity of the oscillating detector.

The range of possible applications of nuclear quadrupole resonance could be greatly extended if signal generators of essentially less internal noise than the existing oscillating detectors could be devised. It is possible that success in this direction might be achieved by circuits with parametric excitation of oscillations, similar to Konstantinov's circuit [27].

An interesting variation of experiments in the NQR field was provided by work on quadrupole spin echo [28,29]. If two rectangular radiofrequency pulses separated by time τ are applied to the specimen, then 2τ seconds after the first pulse an echo signal is produced in the specimen, caused by interaction of the damping signals of nuclear induction from the first and second pulses. Damping of the echo with known τ makes it possible to determine the time T_2 of spin–spin relaxation, and the relationship between the echo amplitude and the time τ between the pulses makes it possible to determine the spin–lattice relaxation time T_1 [17]. Searches for unknown signals by this technique have so far proved unsuccessful.

3. Experiments on Zeeman Splitting of NQR Spectra

Substances, single crystals of which have been studied by the NQR method with application of a weak constant magnetic field, are listed below:

Br^{81} (solid)	[21]	$NaClO_3$	[39]
I^{127} (solid)	[30]	$KClO_3$	[39]
$p\text{-}Cl_2C_6H_4$	[31]	$Ba(ClO_3)_2 \cdot H_2O$	[39]
$p\text{-}Br_2C_6H_4$	[32]	BBr_3	[40]
$p\text{-}ClC_6H_4NH_2$	[11,33]	AsI_3	[41]
$p\text{-}ClC_6H_4CH_2Cl$	[34]	$AsI_3 \cdot 3S$	[41]
$(ClCN)_3$	[35–37]	HIO_3	[42]
$1,2,4,5\text{-}Cl_4C_6H_2$	[38]	Cu_2O*	

The most systematic investigation of Zeeman splitting of NQR spectra was that carried out by Dean et al. [38] in the case of 1,2,4,5-tetrachlorobenzene. Specially designed semiautomatic equipment was used, whereby it was possible to investigate fully the crystal structure of the material. The authors concluded that quadrupole resonance may prove of great help in x-ray structural investigations of certain substances. The accuracy in determinations of bond directions proved to be somewhat better than by the x-ray method; the error did not exceed $\pm 1°$.

Most investigations of Zeeman splitting of NQR signals for chlorine are undertaken for determination of the asymmetry parameter η, because (see Part I of this review), without experimental determination of η, data provided by quadrupole spectra on the nature of chemical bonds are too indefinite.

An interesting example of the use of values of η found by quadrupole resonance is provided by the work of Casabella and Bernes [43]. They succeeded in correlating the values of field gradient asymmetry parameter η_M in the center of the metal atom nucleus, measured for $AlBr_3$ and InI_3, with the valence bond angles formed by the metal atom with halogen atoms in dimeric molecules. The values of bond angles in $AlBr_3$ and InI_3 found from quadrupole resonance data were in quite satisfactory agreement with the values of the valence angles determined from x-ray diffraction data. This also apparently confirmed the bond hybridization model which forms the basis for interpretation of the values of η_M. Unfortunately, these authors apparently did not consider the

*Measured by I. A. Safin.

degree of certainty to which a particular hybridization model is determined in such experiments. However, the calculation idea is itself very valuable, because it is only by correlation of data on nuclear quadrupole interaction with data obtained by independent methods that any reliable information on electron distribution in the molecules of substances can be obtained. In general, it is probably preferable not to predetermine the form of the wave function, but to derive it to a certain degree of reliability in accordance with the experimental parameters (see Part I, Section 7).

4. Chemical Applications of NQR Spectra

It is evident from the example just given that, in many cases, charge distributions in molecules can be investigated in adequate detail by means of quadrupole resonance. Dewar and Lucken [44] point out that the information provided by NQR spectra on charge distribution is often unique, as it cannot be obtained by any other investigation method known at the present time.

These workers [44] investigated π-bonds in chloro derivatives of nitrogen heterocycles. They also studied the character of C–Cl bonds in chloro derivatives of maleic anhydride, thiophene, and aniline salts [45]. In particular, they showed that the NQR frequencies of 2-chlorothiophene, 2,5-dichlorothiophene, and 2,3,4,5-tetrachlorothiophene are considerably higher than those of the corresponding chlorobenzenes (see table of NQR spectra). Dewar and Lucken concluded that the electronegativities of S and C cannot be assumed equal, as is usually done. They suggested that the effective electronegativity of the S atom in chlorothiophenes increases by transfer of one 3p-electron to the 3d-orbit. The C–Cl bond should then become less ionic in character, i.e., the NQR frequency of chlorine should increase; this is found to be the case. This example is an apt illustration of the range of ideas used in interpretation of chemical shifts of quadrupole resonance frequencies. The full table of NQR frequencies in various compounds, which is given in this review, offers the reader a wide field for such correlations and conclusions.

The linear relationship, discovered by Meal [46], between quadrupole frequencies in certain compounds and values of Hammett's constant σ, is of considerable interest with regard to chemical applications of quadrupole resonance. It will be remembered that the semiempirical equation derived by Hammett in 1935 [47] is of the form

$$\ln \frac{k}{k_0} = \sigma\rho, \tag{3}$$

where k is the rate constant of a reaction proceeding in the meta- or para-position to a given substituent in the benzene ring; k_0 is the rate constant for the same reaction in unsubstituted benzene; σ and ρ are constants, the first of which characterizes the influence of the substituent, and the second is general for all substituted benzenes and is characteristic of the reaction. It was pointed out a long time ago [47] that σ is a measure of electron density changes at the site of the reaction, due to the substituent, while ρ measures the "sensitivity" of a given reaction to variations of electron density.

Meal [46] found that the quadrupole resonance frequencies of chlorine in various substituted chlorobenzenes vary linearly with the Hammett constant σ for a given position.

The results of Meal's investigations are shown in Fig. 8. It can be seen that the linear relationship between NQR frequency and σ is only very roughly approximate. It seemed likely that deviations from this relationship should prove no less important for chemical applications of NQR than the general relationship postulated by Meal. Bray's group, which works very productively in the NQR field, has devoted its efforts to attempts to interpret these deviations; a similar trend is characteristic of the work of Dewar and Lucken.

In a large series of investigations by Bray et al. [48-53], the approximate linear relationship between Hammett's constant σ and quadrupole resonance frequencies was confirmed for a very large number of substituted benzenes. The following formula for observed NQR frequencies was derived for various chlorobenzenes:

$$\nu_{obs} = (34{,}826 + 1{,}024\sigma)\ \text{Mc/sec} \tag{4}$$

and for bromobenzenes

$$\nu\,(Br^{81})_{obs} = (227{,}02 + 7{,}866\sigma)\ \text{Mc/sec} \tag{5}$$

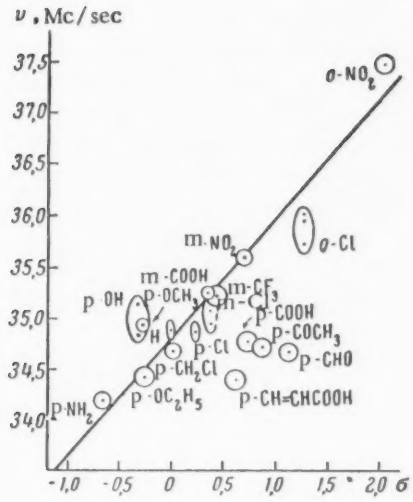


Fig. 8. Relationship between NQR frequencies in various chlorobenzenes with the Hammett constant σ.

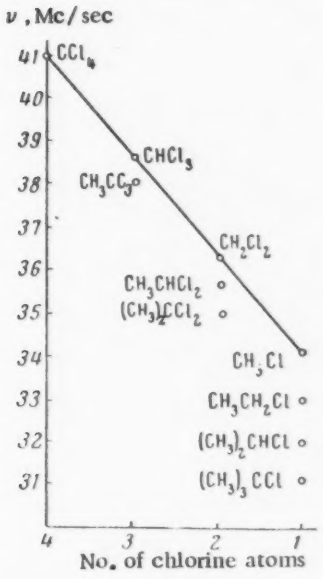


Fig. 9. NQR frequencies of chlorine in certain chloro alkanes.

The importance of these expressions cannot be overestimated: on the one hand, they show that it is possible to predict reactivities of various compounds from their NQR frequencies and, on the other, they offer a deeper insight into the relationship between charge distribution in a molecule and reactivity.

Bray et al. [51] attempted to apply Eqs. (1) and (2) to nitrogenous heterocycles, and attributed the observed deviations from linearity to increase of the double-bond character owing to introduction of nitrogen into the benzene ring. If this course is followed consecutively, large deviations between theory and experiment are found. These deviations may be caused either by the unjustified use for heterocycles of the values of σ obtained in experiments with substituted benzenes, or by the fact that the assumption of additivity of values of σ is invalid.

It must be emphasized that the failure of any particular model "explaining" the influence of different chemical environments on the NQR frequency does not justify pessimistic conclusions on the potentialities of the method. The most important fact is that the influence, which cannot always be explained as yet, exists, and is a powerful effect which shifts the NQR lines by hundreds of kilocycles per second, which is tens, or hundreds of times the half-width of the line. The evident conclusion that these frequency shifts are manifestations of relationships well known to chemists, is important. For example (see Table 1), the NQR frequencies in chloro-, bromo-, and iodosubstituted nitrobenzenes are always higher than in the corresponding halogen-substituted anilines, etc. The high precision to which weak manifestations of such polar influences of various substituent groups can be measured by means of NQR is significant. Similar empirical relationships were discovered by Livingston [54] for chloro alkanes. The NQR frequencies for a number of compounds studied by him are shown in Fig. 9.

Livingston attributes the linear increase of frequency in substituted methanes in the CCl_4 direction to the fact that replacement of hydrogen by the more electronegative chlorine makes the C–Cl bond less ionic in character. Further, an examination of the frequency shifts in Fig. 9 leads to the conclusions that replacement of hydrogen by the CH_2Cl group has little effect on NQR frequency, that the CCl_3 group is close to the Cl atom in electronegativity, that the CH_2Cl group has lower electronegativity, that the CH_2Cl group is close to hydrogen in electronegativity, and that CH_3 is more electropositive than hydrogen. It is easily seen in Fig. 9 that with a fixed number of Cl atoms in the molecule, lengthening of the aliphatic chain influences the NQR frequency to an extent which diminishes with the distance between the successive added CH_3 group and the chlorine atom. This leads to the relationship, shown schematically in Fig. 10, between NQR frequency and chain length (number of C atoms).

The interesting experimental fact, that ortho-neighbors exert a characteristic influence on NQR of Cl^{35} in chlorobenzenes, is examined in [55-56]. For example, in 1,2,3-trichlorobenzene, the NQR frequencies of the

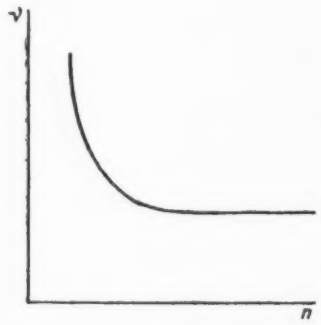


Fig. 10. Variation of the NQR frequency of chlorine with the number n of chlorine atoms in the aliphatic molecule.

chlorine atoms in positions 1 and 3 are lower by 670 kc/sec than that of the intermediate chlorine atom. The difference between these atoms is evidently that each of the first two has one neighboring Cl atom in the ortho-position, whereas the third has two such Cl atoms. Analogous differences of NQR frequencies are found between Cl atoms without any ortho-neighbors and each with one Cl atom in the ortho-position. Duchesne and Monfils [55] attribute these facts to disturbance of the plane character of the chlorobenzene molecule when the Cl atoms are in the ortho-position. If the chlorobenzene molecule is plane, then the C–Cl bond has a considerable proportion of π-character, and this, as we know, lowers the NQR frequency. According to Duchesne and Monfils, removal of the C–Cl bond from the plane of the benzene ring should diminish this π-bonding and hence raise the NQR frequency.

However, Bray et al., showed that, in reality, the double-bond character of the C–Cl bond increases when it is moved through an angle φ out of the ring plane, because the decrease of π-orbit overlapping, which is proportional to $\cos\varphi$, is more than compensated by increased overlapping of the σ-orbits, which is proportional to $\sin\varphi$. Then the increase of the NQR frequency on entry of a neighboring Cl atom into the ortho-position should be attributed to a decrease in the ionic character of the C–C σ-bond, such as was observed by Livingston for chloro alkanes; this decrease of ionic character should preponderate over the frequency decrease caused by increase of double-bond character.

Independent confirmation that the treatment of Duchesne and Monfils is erroneous is provided by the results of an x-ray structural investigation of hexachlorobenzene, conducted by Strel'tsova and Struchkov [57]. The molecule of this compound in the crystal was found to be plane, whereas Duchesne and Monfils were forced to ascribe a value of 25° to the angle φ for hexachlorobenzene in order to explain the observed frequency shifts.

This example confirms once again that it is necessary to compare NQR data with results obtained by other methods. However, the question of the form of the hexachlorobenzene molecule and the percentage of double-bond character in the C–Cl bonds can also be solved by the NQR method by investigations of a single crystal in a weak constant magnetic field (see Section 3).

In addition to the influence of ortho-neighbors, Bray et al. [56], showed that the NQR frequency (with a given number of ortho-neighbors) increases linearly with the number of Cl atoms attached to the benzene ring. This result is explained exclusively by the decrease in the ionic character of the C–Cl bond when an additional Cl atom is attached to the ring.

Thus, despite the absence of a precise theory, work on the chemical applications of NQR has yielded much experimental data in a few years, and has revealed a number of interesting empirical relationships. Much work remains to be done in this field. To aid future searches and correlations, the authors of this review have assembled data on all measurements of NQR frequencies in various compounds known to them as of the summer of 1960. Omissions in the appended table of NQR spectra are possible, but they are probably few.* In general, we give the frequencies at 77°K, so as not to make the table too large. If data for some other temperature are given, this means either that no values at 77°K are available, or that some interesting fact associated with the effect of temperature on quadrupole frequencies is present. In several cases we have used this table for successful prediction of unknown NQR frequencies for chlorine and bromine compounds, by comparison with frequencies of analogous substances containing other halogens. In addition, the relationship illustrated in Fig. 10, and a number of other facts, have been established by means of this table. Some of these facts are discussed below.

5. NQR Spectra and the Structure of Solids

Even the earliest work on quadrupole resonance revealed the high sensitivity of the method to crystal effects. These effects are: a) splitting of NQR lines owing to nonequivalence of the positions of the molecule in

*The frequencies of more than 100 compounds are given in a fundamental paper by Hooper and Bray [J. Chem. Phys. 33, 334 (1960)].

the lattice; b) line broadening due to crystal-lattice imperfections; c) influence of thermal motion in the crystal on the frequency and form of the line. In the table of NQR spectra, the reader will find numerous examples showing that crystal shifts of NQR frequencies are usually much greater than the line width, and their measurements make no special demands on the resolving power of the instrument.

In chemical investigations such crystal splitting is a hindrance, as it makes interpretation of the results difficult and, in many cases, gives rise to doubt whether the observed effect is of chemical origin. There is an empirical upper limit of crystal effects for every range of quadrupole frequencies. For example, Dewar and Lucken [45] consider that, in the case of NQR of chlorine frequency, shifts up to 500 kc/sec may be of crystal origin, while all shifts greater than 500 kc/sec can be, with confidence, ascribed to various chemical factors. Unfortunately, first, it is difficult to find any serious justification for this particular restriction of the range of crystal effects; and, second, in a fairly large number of cases effects of undoubted chemical origin are smaller, such as the chemical shifts in many chlorobenzenes. Estimates with the aid of Eq. (7) (see below) indicate that, apparently, in some cases, we may find crystal splitting of the NQR lines of the order of 10% of the frequency, i.e., 2-3 Mc/sec in the chlorine band and 10-20 Mc/sec in the bromine and iodine bands. It may be that it is this that accounts for the splitting observed for $O_2IC_6H_5$ ($\Delta\nu$ = 18.4 Mc/sec), 2,6-dibromo-4-nitrophenol ($\Delta\nu$ = = 13.7 Mc/sec), $O_2(CHCl)_4$ ($\Delta\nu$ = 2.1 Mc/sec), and certain other compounds (see Table 1).

It is therefore clear that elucidation of the main relationships between crystal structure and NQR signals is of fundamental importance for putting the chemical applications of quadrupole spectra on a firm basis. It is also quite evident that quadrupole resonance may prove a powerful weapon for investigating a number of problems on the physics of solids as such. Here the influence of thermal vibrations and defects in real crystals on NQR is especially important.

It was already stated in the first part of this review that a theory of crystal effects in NQR can be formulated only after the laws of intermolecular interaction have become known. Much work has recently been done in this field, showing that there are real prospects of investigating and understanding certain relationships between intermolecular interaction and quadrupole resonance in molecular crystals.

It may be assumed a priori that the fundamental principles of organic crystal chemistry [58], established on the basis of very extensive experimental data, would prove useful in studies of crystal effects in NQR spectra of organic compounds. The facts support this assumption. On the other hand, it is quite reasonable to hope that the extreme sensitivity of NQR to perfection of the crystal lattice would make it possible to define more closely the concepts of organic crystal chemistry on molecular interaction in crystals.

Influence of Crystal Imperfections on NQR. Many studies have been concerned with the effects of various distortions of the crystal lattice on quadrupole resonance signals. Two methods are used in such investigations: either the crystal is subjected to the action of γ-, β-, or neutron radiation [59-61], or the lattice is deformed by formation of substitutional solid solutions [61-70]. In either case, the amplitude of the NQR signal is lowered.

The rate at which the signal amplitude falls with increase of the absorbed radiation dose is a measure of the radiation stability of the specimen. According to Duchesne [59], the measure of the radiation stability of a crystal to the action of γ-radiation is the dose which reduces the intensity of the NQR signal by 40%. He also showed that the signal amplitude decreases roughly exponentially with increase of the dose. However, this relationship breaks down at high doses; the decrease of the NQR signal slows down and eventually almost ceases with increase of the dose. This observation has been checked and confirmed [60, 61]. Kitaigorodskii and Fedin [60] offered the following explanation for this fact: irreversible chemical changes take place in defective regions of the crystal, and the molecular fragments are packed more loosely during the filling of voids than the molecules in the lattice of a nonirradiated crystal. After all the voids in the crystal have been filled with radiolysis products, the average mobility of the molecular fragments over the crystal drops sharply and further increase of the dose has little effect on the amplitude of the NQR signal. Simple calculations based on this model can be used for estimating block dimensions and the volume percentage of voids in the crystal from experimental data. The concepts used in [60] inevitably led to the conclusion that a carefully grown single crystal should have much higher radiation resistance than an ordinary crystal, and still more than a polycrystalline specimen. This conclusion was experimentally confirmed quite independently by Adler [71], who used a different method. Thus, the theory of close packing of organic molecules in crystals [58] proved fruitful in the solution of certain problems of NQR spectroscopy.

TABLE 1

Substance	NQR frequencies, Mc/sec	Temp, °K	Literature sources and other data (eqQ, Mc/sec)
1	2	3	4
	I. Cu^{63-65}		
	Cu – C bond		
$K[Cu(CN)_2]$	$\nu_1 = 32,661$	298	[83]. ν_1 and ν_2 refer to the Cu^{63} and Cu^{65} isotopes, respectively
	$\nu_2 = 30,221$		
	Cu – O bond		
$Cu_2^{63}O$	26,697	298	[83]
	II. Hg^{201}		
	Hg – Cl bond		
$Hg^{201}Cl_2$	361,966	83	[84]
	III. B^{10-11}		
B^{11}	2,695	298	[85] $eqQ_{B^{11}} = 5.39$
	B – C bond		
$B^{11}H_3CO$	0,775	298	[85] $eqQ = 1,55$
I.$B(CH_3)_3$	$\nu_1 = 1,5225$	83	[86]. ν_1 and ν_2 in both I and II refer to B^{10}, ν_3 refers to B^{11}; I and II are two crystalline modifications, with a phase transition, lasting several hours, at 112°K
	$\nu_2 = 2,5378$	83	
	$\nu_3 = 2,4367$	83	
II.$B(CH_3)_3$	$\nu_1 = 1,5536$	83	
	$\nu_2 = 2,5890$	83	
	$\nu_3 = 2,4845$	83	
$B(C_2H_5)_3$	$\nu_1 \begin{cases} = 1,5554 \\ = 1,5740 \end{cases}$	83	[86]. ν_1 (doublet) and ν_2 refer to B^{10}; ν_3 refers to B^{11}
	$\nu_2 = 2,6068$	83	
	$\nu_3 = 2,5016$	83	
	B – O bond		
$Na_2B_4^{11}O_7 \cdot 4H_2O$	$\nu_1 = 1,286$	296,89	[78]. $\eta_1 = 16,3\%$; $\eta_2 = 11,7\%$
	$\nu_2 = 1,287$		
	IV. Al^{27}		
	Al – Br bond		
$AlBr_3$	$\nu_1 = 3,0319$	77	[43]. ν_1 and ν_2 correspond to the transitions $\pm 1/2 \rightarrow \pm 3/2$ and $\pm 3/2 \rightarrow \pm 5/2$, respectively. $\eta = 72,85\%$, eqQ = 13,858
	$\nu_2 = 3,8326$	77	
	V. Ga^{69-71}		
	Ga – Cl bond		
$GaCl_3$	$\nu_1 = 29,060$	304,8	[88]. ν_1 and ν_2 refer to Ga^{69} and Ga^{71}, respectively
	$\nu_2 = 18,315$		
	Ga – Br bond		
$Ga^{69}Br_3$	26,494	77	[89]
	Ga – I bond		
$Ga^{69}I_3$	21,441	298	[89]
	VI. In^{115}		
	In – I bond		
InI_3	$\nu_1 = 37,506$	298	[89]. $\eta = 69,0\%$;
	$\nu_2 = 26,985$	298	eqQ = 320.41; ν_1, ν_2, ν_3, and ν_4 correspond to the transitions $\pm 1/2 \rightarrow \pm 3/2$,
	$\nu_3 = 36,265$	298	$\pm 3/2 \rightarrow \pm 5/2$,
	$\nu_4 = 51,238$	298	$\pm 5/2 \rightarrow \pm 7/2$,
	$\nu_5 = 63,2$	298	$\pm 1/2 \rightarrow \pm 1/2$; and $\pm 1/2 \rightarrow 9/2$; ν_5 refers to the "forbidden" $\pm 3/2 \rightarrow \pm 7/2$ transition. Also, see [150].
	VII. N^{14}		
	N – H bond		
NH_3	2,6779	77	[90] $eqQ = 3,5705$

TABLE 1 (continued)

1	2	3	4
ND_3	2,4231	77	[90] $eqQ = 3,2308$
	N – C bond		
$(CH_3)_3N$	3,8954	77	[90] $eqQ = 5,1939$
$(CH_2)_6N_4$	3,4076	77	[91] $\eta = 0$
$CO(NH_2)_2$	$\nu_1 = 2,347$	77	[92] $\eta = 32,3\%$;
	$\nu_2 = 2,9137$		eqQ = 3,507; ν_1 and ν_2 refer to splitting of levels owing to the high asymmetry parameter (the spin of N^{14} is 1)
$p\text{-}(NH_2)_2C_6H_4$	$\nu_1' = 2,674$		[99]. ν_1 and ν_2 correspond to splitting of levels owing to the high asymmetry parameter; ν', ν'', ν''' appear as the result of the crystallographically nonequivalent positions of the nitrogen atoms; eqQ = 3,910 and η = 26.4% (average values for crystallographic positions)
	$\nu_1'' = 2,690$	77	
	$\nu_1''' = 2,694$		
	$\nu_2' = 3,1902$		
	$\nu_2'' = 3,2109$	77	
	$\nu_2''' = 3,2129$		
$p\text{-}ClC_6H_4NH_2$	2,837	77	[92]. $eqQ = 4,117$;
	3,382	77	$\eta = 24,3\%$
$p\text{-}BrC_6H_4NH_2$	2,860	77	[92]. $eqQ = 4,135$;
	3,3417	77	$\eta = 23,1\%$
HCN	3,0223	77	[93]. $eqQ = 4,0183$;
	3,0052	77	$\eta = 0,85\%$
ClCN	2,400	77	[94]
	2,428	77	
BrCN	2,5109	77	[91,95]
	2,5203	77	
ICN	2,5424	299,8	[20,91]
CH_3CN	2,8078	77	[52]. $eqQ = 3,7380$
	2,7992	77	[93]. $\eta = 0,46\%$
$CH_2(CN)_2$	$\nu_1 = 3,0154$	77	[52]. $eqQ = 3,9216$;
	$\nu_2 = 2,8670$	77	$\eta = 7,57\%$
$(CNCl)_3$	$\nu_1 = 3,0445$	77	[96] $eqQ = 4,083$;
	$\nu_2 = 3,0799$	77	$\eta = 1,7\%$
	VIII. As^{75}		
	As – C bond		
$As(C_6H_5)_3$	$\nu_1 = 98,900$	77	[97]. ν_1 and ν_2 are due to the crystallographically nonequivalent positions of the arsenic atoms
	$\nu_2 = 98,500$	77	
	As – O bond		
As_2O_3	116,781	77	[98,99]
	As – Cl bond		
$AsCl_3$	78,950	77	[97,100]
	As – Br bond		
$AsBr_3$	63,569	83	[97,101]
	As – I bond		
AsI_3	29,338	77	[97,100]
$AsI_3 \cdot 3S_8$	49,501	77	[100]
	IX. Nb^{93}		
	Nb – O bond		
$KNbO_3$	$\nu_1 = \ldots$*		
	$\nu_2 = 1,335$		[102]. ν_1, ν_2, ν_3, and ν_4 correspond to the transitions:
	$\nu_3 = 2,004$	77	$\pm 1/2 \rightarrow \pm 3/2$, $\pm 3/2 \rightarrow \pm 5/2$,
	$\nu_4 = 2,674$		$\pm 5/2 \rightarrow 7/2$, and $\pm 7/2 \rightarrow \pm 9/2$;
$KNbO_3$	$\nu_1 = 3,030$		eqQ = 16.0 (77°K) and 23.12 (298°K);
	$\nu_2 = 2,085$		η = 0 (77°K) and 80.6% (298°K)
	$\nu_3 = 2,527$	298	

*Here and subsequently, "$\nu = \ldots$" indicates that a line probable on theoretical grounds has not been detected experimentally.

TABLE 1 (continued)

1	2	3	4
	ν_4=3,648		
	X. $Sb^{121-123}$		
	Sb – C bond		
$Sb(C_6H_5)_3$	ν'_1=156,200		[103]. Doublets ν_1 & ν_2 correspond to the transitions $\pm 3/2 \rightarrow$
	ν''_1=152,471	77	$\rightarrow \pm 5,2$ & $\pm 1/2 \rightarrow \pm 3/2$, associated with Sb^{121}; doublets ν_3,
	ν'_2= 78,274		ν_4 and ν_5 correspond to
	ν''_2= 76,912		$\pm 5/2 \rightarrow \pm 7/2$,
	ν'_3=142,174		$\pm 3/2 \rightarrow \pm 5/2$
	ν''_3=138,859		$\pm 1/2 \rightarrow \pm 3/2$, associated with Sb^{123}.
	ν'_4=94,741		Doublets arose owing to crystallographically nonequivalent positions
	ν''_4= 92,267		of the antimony atoms.
	ν'_5= 47,841		For Sb^{121} lines
	ν''_5= 47,545		$(eqQ)' = 520,84$; $\eta' = 2,6\%$,
			$(eqQ)'' = 509,00$: $\eta'' = 8,0\%$.
			For Sb^{123} lines
			$(eqQ)' = 664,18$, $\eta' = 1,8\%$,
			$(eqQ)'' = 648,56$, $\eta'' = 8,3\%$
$Sb(C_3H_7O)_3$	ν_1=167,570	77	[103]. ν_1 & ν_2 correspond to the transitions
	ν_2= 85,804		$\pm 3,2 \rightarrow 5/2$ &
	ν_3=...		$\pm 1/2 \rightarrow \pm 3/2$ for Sb^{121};
	ν_4=101,111		$(eqQ)_{121} = 560,66$,
	ν_5=...		$\eta_{121} = 13,8\%$
			ν_4 – to transition $\pm 3/2 \rightarrow 5/2$ for Sb^{123}.
	Sb – O bond		
Sb_2O_3	ν_1=166,45	77	[13,104] ν_1 & ν_2 – lines for Sb^{121};
	ν_2= 83,21		ν_3, ν_4 & ν_5 – lines for Sb^{123};
	ν_3=151,89		$(eqQ)_{121} = 554,83$; $\eta_{121} \approx 0$;
	ν_4=101,01		$(eqQ)_{123} = 707,11$; $\eta_{123} \approx 0$
	ν_5=50,511		
	Sb – S bond		
Sb_2S_3	ν_1=88,66300	303,75	[8]. ν_1 & ν_2 – lines for Sb^{121}; ν_4
	ν_2=44,33480		& ν_5 – lines for Sb^{123};
	ν_3=...		$(eqQ)_{121} = 295,54679$;
	ν_4=53,81785		$\eta_{121} = 0,76\%$;
	ν_5=26,91568		$(eqQ)_{123} = 376,73771$; $\eta_{123} = 0,77\%$
	Sb – Cl bond		
$SbCl_3$	ν_1=114,300	83	[8,103 – 105] ν_1 & ν_2 – lines for
	ν_2= 59,709		Sb^{121}; ν_3, ν_4 & ν_5 – lines for Sb^{123};
	ν_3=104,460		$(eqQ)_{121} = 383,69$; $\eta_{121} = 18,9\%$;
	ν_4= 68,648		$(eqQ)_{123} = 489,34$; $\eta_{123} = 18,7\%$
	ν_5= 39,094		
	Sb – Br bond		
$SbBr_3$	ν_1=99,215	77	[8,100] ν_1 & ν_2 – lines for Sb^{121};
	ν_2=50,273		ν_4 & ν_5 – lines for Sb^{123};
	ν_3=...		$(eqQ)_{121} = 343,95$; $\eta_{121} = 10\%$;
	ν_4=60,107		$(eqQ)_{123} = 422,987$; $\eta_{123} = 9,5\%$
	ν_5=31,186		
	Sb – I bond		
SbI_3	ν_1=...		[100]. ν_5 – line for Sb^{123} corresponding
	ν_2=...		to the transition $\pm 1/2 \rightarrow$
	ν_3=...	77	$\rightarrow \pm 3/2$; $(eqQ)_{123} \approx 169,37$
	ν_4=...		
	ν_5=25,406		
$SbI_3 \cdot 3S_8$	ν_5=37,461	297	[100]. ν_5 – line for Sb^{123}, corresponding to the transition $\pm 1/2 \rightarrow$
			$\rightarrow \pm 3/2$; $(eqQ)_{123}$ 249.74
	XI. Bi^{209}		
	Bi – C bond		
$Bi(C_6H_5)_3$	ν_1= 29,785		[106]. ν_1, ν_2, ν_3, and ν_4 correspond

TABLE 1 (continued)

1	2	3	4
	ν_2= 55,214 ν_3= 83,516 ν_4=111,438	83	to the transition $\pm 1/2 \rightarrow \pm 3/2$, $\pm 3/2 \rightarrow \pm 5/2$, $\pm 5/2 \rightarrow \pm 7/2$ и $\pm 7/2 \rightarrow \pm 9/2$; eqQ=669,06 $\eta \approx 9\%$
	Bond Bi — Cl		
$BiCl_3$	ν_1=33,726 ν_2=25,905 ν_3=37,900 ν_4=52,704	83	[107]. ν_1, ν_2, ν_3 & ν_4 correspond to the transitions $\pm 1/2 \rightarrow \pm 3/2$, $\pm 3/2 \rightarrow \pm 5/2$, $\pm 5/2 \rightarrow \pm 7/2$ & $\pm 7/2 \rightarrow \pm 9/2$; eqQ=325,5; η=58,3%
	XII. S^{33}		
S_8	22,801 22,866 22,896 22,964	298	[108]. Multiplet character (4 lines) due to nonequivalent positions of sulfur atoms in the crystal
	XIII. Cl^{35-37}		
	Bond Cl — H		
HCl^{35}	26,695	20	[54]
	Bond Cl — Hg		
$HgCl_2$	ν'_1=22,2303 ν''_1=22,0503 ν'_2=17,5197 ν''_2=17,3789	303	[84]. The doublet ν_1 corresponds to Cl^{35} ; the doublet ν_2 to Cl^{37}
	Bond Cl — B		
BCl_3	ν'_1=21,582 ν''_1=21,578 ν'_2=17,008 ν''_2=17,004	77	[40]. The doublet ν_1 corresponds to Cl^{35} ; the doublet ν_2 to Cl^{37}
	Bond Cl — Ga		
$GaCl_3$	ν'_1=20,225 ν''_1=19,084 ν'''_1=14,667 ν'_2=15,935 ν''_2=15,040 ν'''_2=11,562	306,2	[88]. ν_1 corresponds to Cl^{35} , ν_2 to Cl^{37}. The multiplet character is due to nonequivalence in the crystal. ν''_{1-2} is very distinct from ν'_{1-2} and ν''_{1-2} due to dimerization.
	Bond Cl — C		
CF_2BrCl	38,342 38,675	77 20	[54]. Cl^{35}
CF_3Cl	38,089 38,790	77 20	[54]. Cl^{35}
$COCl_2$	36,225 36,081	77	[54,63]. Cl^{35} [54]. Cl^{35}
CF_2Cl_2	38,450 39,078	77 20	
CCl_4	40,465 40,521 40,540 40,549 40,576 40,587 40,607 40,639 40,643 40,655 40,696 40,721 40,782 40,797 40,817	77	[54, 109, 110, 111]. Cl^{35}. Multicomponent nature due to nonequivalent positions of chlorine atoms in crystal

TABLE 1 (continued)

1	2	3	4
$CHCl_3$	ν_1=38,254 ν_2=38,308	77	[54, 109, 111]. ν_1 and ν_2 correspond to crystallographically non-equivalent atoms of Cl^{35}
$CHFCl_3$	36,7	20	[112]. Cl^{35}
CHF_2Cl	35,2	20	[112]. Cl^{35}
CH_2FCl	33,799	20	[54]. Cl^{35}
CH_2Cl_2	35,991	77	[54, 109, 11].Signal Cl^{35}
CH_3Cl	ν_1=34,029 ν_2=26,81552	77	ν_1 measured in [54] for Cl^{35}; ν_2 measured in [8] for Cl^{37}
Cl_3CCOCl	ν_1=40,613 ν_2=40,473 ν_3=40,132 ν_4=33,721	77	[113]. ν_1 to ν_3 correspond to chlorine atoms in methyl group; ν_4 to chlorine in group COCl
ClOCCOCl	33,621	77	[114]. Cl^{35}
Cl_3CCN	41,7296 41,6660 41,5340	77	[115]. Cl^{35}
Cl_3CCCl_3	40,761 40,714 40,685 40,551 40,885 40,823 40,798 40,652	77 20	[54]. Cl^{35}
$ClCF_2COOH$	37,485	77	[116]. Cl^{35}
$CFCl_2COOH$	39,594	77	[116]. Cl^{35}
Cl_2CHCF_3	38,694	77	[116]. Cl^{35}
$Cl_2HCCOCl$	ν_1=39,386 ν_2=39,189 ν_3=38,521 ν_4=38,353 ν_5=32,962 ν_6=32,147	77	[114]. Cl^{35}; $\nu_1 - \nu_4$ correspond to chlorine atoms in methyl group; ν_5 and ν_6 to chlorine atom of COCl. ν_1 and ν_2, ν_3 and ν_4, ν_5 and ν_6 are doublets caused by crystallographic factors
Cl_3CCOOH	40,240 40,165 39,967	77	[113]. Cl^{35}
$Cl_2CHCOOH$	38,807 37,979	77	[113]. Cl^{35}
$CH_2ClCOCl$	ν_1=37,517 ν_2=30,437	77	[114]. Cl^{35}; ν_1 corresponds to chlorine in methyl group; ν_2 —to chlorine of the COCl group
Cl_2CHCN	40,0840 39,9233 39,7537 39,4434	77	[115].Cl^{35}
Cl_2CHCCl_3	39,862 39,836 39,758 38,759 38,711 39,988 39,954 39,923 38,888 38,852	77 20	[54]. Cl^{35}
$ClCH_2COONa$	34,794	77	[113]. Cl^{35}
$ClCH_2CN$	38,1251	77	[115]. Cl^{35}
cis-ClCH = CHCl	35,029 34,968	20	[54]. Cl^{35}, see also in [42]
trans -ClCH = CHCl	ν_1 = 35,9862 ν_2 = 28,3646	77	In [8] ν_1 corresponds to Cl^{35}, ν_2 — Cl^{37}. In [54], [56] the NQR

TABLE 1 (continued)

1	2	3	4
	35,584	20	frequency was measured at 20°K; measurements also in [117].
Cl_3CCONH_2	40,007		[113]. Cl^{35}. At 196°K, only three lines found instead of six; this indicates a phase transition in the 77-196°K range
	39,817		
	39,665	77	
	39,599		
	39,478		
	38,850		
	39,528		
	39,229	196	
	39,106		
$ClCH_2COOH$	36,131	77	[113]. Cl^{35}
	36,429		
$Cl_2CHCONH_2$	37,750	77	[118]. Cl^{35}
	37,238		
CH_2-$CHCl$	33,61	20	[56]. Cl^{35}
CH_3CCl_3	38,052	77	[109]. Cl^{35}
	37,829		
$Cl_3CCH(OH)_2$	39,515		[113]. Cl^{35}
	39,429	77	
	38,190		
$ClCH_2CONH_2$	34,882	77	[113]. Cl^{35}
$ClCH_2CH_2Cl$	34,361	77	[54]. Cl^{35}
	34,442	20	
CH_3CHCl_2	35,55	20	[112]. Cl^{35}
$ClCH_2OCH_2Cl$	32,381	77	[54]. Cl^{35}
	32,587		
$ClCH_2SCH_2Cl$	34,749	77	[116]. Cl^{35}
	34,526		
C_2H_5Cl	33,5	20	[112]. Cl^{35}
$ClCH_2OCH_3$	30,181	77	[116]. Cl^{35}
$ClCH_2SCH_3$	33,104	77	[116]. Cl^{35}
CH_2-$CHCH_2Cl$	33,753	86	[116]. Cl^{35}
$ClCH_2COCH_3$	35,075	77	[113]. Cl^{35}
	35,484		
$ClOCOC_2H_5$	33,858	77	[119]. Cl^{35}
$Cl_3CCH(OH)OCH_3$	38,59		[120]. Cl^{35}
	38,74	90	
	38,83		
$CH_3CCl_2CH_3$	34,883	77	[54]. Cl^{35}
	35,046	20	
$(CH_3)_2NCOCl$	31,8	77	[118]. Cl^{35}
C_3H_7Cl	35,753	86	[116]. Cl^{35}
$CH_3CHClCH_3$	32,1	20	[112]. Cl^{35}
$CH_3CHClOCH_3$	33,453	77	[116]. Cl^{35}
$Cl-C-C=O$ (with $\|$ and $\diagdown O \diagup$)	37,945	86	[45]. Cl^{35}
	38,013		
$Cl-C-C=O$			
$Cl_2CFCOCFCl_2$	39,312	77	[116]. Cl^{35}
	39,104		
2,4,5,6-Cl_4-1,3-N_2C_4	38,420		[51, 121]. Cl^{35}
	38,020		
	37,068	77	
	36,560		
	36,281		
$F_3CCCl=CClCF_3$	39,491	77	[116]. Cl^{35}
Cl_4C_4S	37,517	86	[45]. Cl^{35}
$Cl-C=C=O$ (with $\|$ and $\diagdown O \diagup$)	37,159	86	[45]. Cl^{35}
$H-C-C=O$			
2,4,6-Cl_3-1,3-N_2C_4H	36,205		[44, 121]. Cl^{35}
	36,166	77	

TABLE 1 (continued)

1	2	3	4
	35,702		
$ClOC(CH)_2COCl$	30,970	77	[114]. Cl^{35}; crystallographic doublet
	30,380		
$4,6\text{-}Cl_2\text{-}1,3\text{-}N_2C_4H_2$	35,425		
	35,308	77	
	35,132		
	35,102		
$2,5\text{-}Cl_2C_4H_2S$	36,669		[45]. Cl^{35}
	36,696	86	
	36,840		
	36,875		
$ClCH_2COCH_2Cl$	35,943	77	[73]. Cl^{35}
	34,824	77	[118]. Cl^{35}
$ClOC(CH_2)_2COCl$	30,217	77	[114]. Cl^{35}
$(C_2H_3Cl_2O)_2$	36,968	77	[118]. Cl^{35}
	34,824		
$Cl_3CCOOC_2H_5$	44,339	77	[119]. Cl^{35}
	40,200		
$2,4\text{-}(NH_2)_2\text{-}6Cl\text{-}1,3\text{-}N_2C_4H$	34,304	77	[121]. Cl^{35}
$CH_2\text{-}CCH_2CH_2Cl$	33,777	77	[116]. Cl^{35}
$ClCH_2COOC_2H_5$	35,962	77	[113]. Cl^{35}
$Cl_3CCH(OH)OC_2H_5$	39,140		[120,122]. Cl^{35}
	38,765	77	
	38,516		
$CH_3CHClOCHClCH_3$	33,392	77	[116]. Cl^{35}
	33,483		
$(CH_3)_3CCl$	31,065	77	[109]. Cl^{35}
	31,195	20	
$1,2\text{—}Cl_2\text{—}3,3,4,4,5,5\text{—}\text{—}F_6C_5$	38,039	77	[116]. Cl^{35}
$2,4\text{-}Cl_2\text{-}1,3\text{-}N_2C_5H_2$	35,321	77	[51,121]. Cl^{35}
	35,310		
	30,726	77	[114]. Cl^{35}
$2\text{-}Cl\text{-}1,3\text{-}N_2C_5H_3$	34,173	86	[44]. Cl^{35}
$2\text{-}ClC_5H_4N$	34,194	77	[123]. Cl^{35}
$3\text{-}ClC_5H_4N$	35,238	77	[51]. Cl^{35}
$4\text{-}ClC_5H_4N$	35,042		[51]. Cl^{35}
	35,031	77	
	34,748		
	34,739		
$3,5\text{-}Cl_2\text{-}C_5H_4N$	35,601	77	[51]. Cl^{35}
$2,4\text{-}Cl_2\text{-}5\text{-}CH_3\text{-}1,3\text{-}N_2C_4H$	35,338		[121]. Cl^{35}
	34,893	77	
$2,4\text{-}Cl_2\text{-}6\text{-}CH_3\text{-}1,3\text{-}N_2C_4H$	35,256	7	[51,121]. Cl^{35}
$4,6\text{-}Cl_2\text{-}2\text{-}CH_3\text{-}1,3\text{-}N_2C_4H$	35,156	8	[44]. Cl^{35}
$2\text{-}Cl\text{-}C_5H_4N\cdot HCl$	37,559	7	[123]. Cl^{35}
$2\text{-}NH_2\text{-}5\text{-}ClC_5H_4N$	35,630	77	[51]. Cl^{35}
$(C_2H_5)_2NCOCl$	31,877	77	[118]. Cl^{35}
$4\text{-}NH_2\text{-}6\text{-}Cl\text{-}2\text{-}CH_3S\text{—}1,3\text{-}\text{-}N_2C_4H$		77	[51, 121]. Cl^{75}
$6\text{-}Cl\text{-}2,4\text{-}(CH_3O)_2\text{—}1,3\text{-}\text{-}N_2C_4H$	34,993	77	[51, 121]. Cl^{35}
	34,618		
$6\text{-}NH_2\text{-}2,4\text{-}Cl_2\text{-}C_2H_5\text{-}1,3\text{-}\text{-}N_2C_4$	34,879	86	[44]. Cl^{35}
	35,044		
$ClOC(CH_2)_4COCl$	28,978	77	[114]. Cl^{35}
$(ClCH_2CHO)_3$	35,363	77	[113]. Cl^{35}
	35,601		
C_6Cl_6	38,403		[55, 124]. Cl^{35}
	38,452	77	
	38,381		

TABLE 1 (continued)

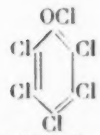
1	2	3	4
$(CNCl)_3$	ν_1=36,7708	77	[36, 44, 51, 110]. ν_1, ν_2, and ν_3 refer to Cl^{35}; ν_4 and ν_5 to Cl^{37}. Asymmetry parameters determined in [37] at 299°K: η_2 = =26%, η_3 = 23%
	ν_2=36,2997		
	ν_3=36,1720		
	ν_4=28,6078	294	
	ν_5=28,6208		
	40,100		[122]. Cl^{35}
	39,997	77	
	38,157		
	37,865		
	37,553		
	37,055		
$2,3,5,6\text{-}Cl_4C_6O_2$	37,585	77	[51]. Cl^{35}
	37,515		
	37,470		
	37,442		
C_6HCl_5	38,153		[56]. Cl^{35}
	37,959		
	37,720	77	
	37,504		
	37,466		
C_6Cl_5OH	38,5794		[125,126]. Cl^{35}
	38,1915	77	
	37,3750		
	37,1292		
$1,2,3,4\text{-}Cl_4C_6H_2$	37,557		[56]. Cl^{35}
	37,455	77	
	37,013		
	37,013		
$1,2,3,5\text{-}Cl_4C_6H_2$	37,657		[56], Cl^{35}
	37,483		
	37,289		
	37,020	77	
	36,872		
	36,816		
	36,386		
	36,185		
$1,2,4,5\text{-}Cl_4C_6H_2$	36,898		[127,128]. Cl^{35}
	36,843		
	36,738	77	
	36,702		
$2,5\text{-}Cl_2C_6H_2O_2$	36,321	77	[51]. Cl^{35}
$2,6\text{-}Cl_2C_6H_2O_2$	36,361		[51]. Cl^{35}
	36,266	77	
$2,5\text{-}Cl_2\text{-}3,6\text{-}(OH)_2\text{-}C_6O_2$	37,148	77	[51]. Cl^{35}
$2,4,6\text{-}(NO_2)_3\text{-}C_6H_2Cl$	39,367	77	[53]. Cl^{35}
$1,2,3\text{-}Cl_3C_6H_3$	37,031		[56,129]. Cl^{35}
	36,973		
	36,523	77	
	36,268		
	36,238		
	36,214		
$1,2,4\text{-}Cl_3C_6H_3$	36,623		[56,130]. Cl^{35}
	36,400		
	36,380	77	
	36,173		
	35,617		
	35,189		
$1,3,5\text{-}Cl_3C_6H_3$	ν_1=36,115		[56]. Cl^{35}. In [57] effect of temperature on NQR frequencies was investigated; found η_1 = 12%, η_2 = 11% & η_3 = 9% at 299°K
	ν_2=35,894	77	
	ν_3=35,545		
$2,4,6\text{-}Cl_3C_6H_2OH$	36,770		[53]. Cl^{35}
	35,400	77	
	35,262		

TABLE 1 (continued)

1	2	3	4
2,5-Cl_2-$C_6H_3SO_2Cl$	37,3200 36,3913 34,4484	77	[126]. Cl^{35}
2,4-$Cl_2C_6H_3NO_2$	ν_1=37,874 ν_2=35,921	77	[125, 131]. Cl^{35}. Presumed that ν_1 corresponds to chlorine in the o-position to the NO_2 group and ν_2 to the m-position
3,4-$Cl_2C_6H_3NO_2$	ν_1=37,055 ν_2=36,488	77	[125]. Cl^{35}. Presumed that ν_1 corresponds to chlorine in the p-position to the NO_2 group, and ν_2 to the m-position
2,4-$(NO_2)_2C_6H_3Cl$	37,796	77	[120,122,132]. Cl^{35}
2,5-$Cl_2C_6H_3SO_2Na$	36,5040 35,2117	77	[126]. Cl^{35}
o-$Cl_2C_6H_4$	35,824 35,580	77	[46]. Cl^{35}
m-$Cl_2C_6H_4$	35,030 35,030 34,875 34,809	77	[46]. Cl^{35}
p -$Cl_2C_6H_4$	ν_1=34,77540 ν_2=27,40811	77	In [8] ν_1 corresponds to Cl^{35} and ν_2 to Cl^{37}. NQR frequencies of p-$Cl_2C_6H_4$ also given in [46, 131,133]. Asymmetry parameter η = 8% at 299° determined in [37]; effect of temperature on relaxation time T_1 found in [73] (at 77°K T_1 = 560 ± 50 sec)
2,6-Cl_2-4-NO_2-$C_6H_2NH_2$	35,920	77	Cl^{35}. Measured by Fedin [127].
2,4,6-$Cl_3C_6H_2NH_2$	35,885 35,780 35,591 35,177 34,976 34,925	77	
o-$ClC_6H_4NO_2$	37,260	77	[14]. Cl^{35}
m -$ClC_6H_4NO_2$	35,457	77	[46]. Cl^{35}
2,6-$(NO_2)_2$-4-Cl-$C_6H_2NH_2$	37,280	77	[53]. Cl^{35}
p -$ClC_6H_4SO_2Cl$	35,967	77	[120]. Cl^{35}. NQR line refers to chlorine in benzene ring.
p -$ClC_6H_4SO_2Na$	35,1366	77	[125.] Cl^{35}
C_6H_5Cl	ν_1=34,6216 ν_2=27,2872	77	[46,54,111]. ν_1 corresponds to Cl^{35}, ν_2— Cl^{37}
m-ClC_6H_4OH	34,825 34,766	77	[53]. Cl^{35}
p -$Cl_6C_6H_4OH$	34,945 34,700	77	[46]. Cl^{35}
2,4-$Cl_2C_6H_3NH_2$	34,854 34,734	77	[53]. Cl^{35}
3,4-$Cl_2C_6H_3NH_2$	35,872 35,673	77	[53]. Cl^{35}
2,5-$Cl_2C_6H_3NH_2$	34,530 34,413	77	[120,131]. Cl^{35}
2,4,6-$Cl_3C_6H_2NHNH_2$	36,235 35,810 35,569	77	[127]. Cl^{35}
m-$ClC_6H_4NH_2$	34,468 34,388	77	[53]. Cl^{35}
p -$ClC_6H_4NH_2$	34,146	77	[46]. Cl^{35}
p -$ClC_6H_4NH_2$·HCl	35,448	86	[58]. Cl^{35}. NQR of chlorine in HCl not detected
p-$ClC_6H_4NH_2$·HBr	34,752	86	[45]. Cl^{35}

TABLE 1 (continued)

1	2	3	4
$2,5\text{-}Cl_2C_6H_3SO_2Cl\cdot 2H_2O$	36,4500		[126]. Cl^{35}
	36,1600	77	
	35,6222		
$2,6\text{-}Cl_2C_6H_6O$	35,501	77	[134]. Cl^{35}
$6,6\text{-}Cl_2C_6H_6O$	ν_1=36,475		[134]. ν_1 & ν_2 refer to Cl^{35}
	ν_2=36,703		ν_3 & ν_4 — C ^{37}
	ν_3=28,769	77	
	ν_4=28,963		
$2,4\text{-}Cl_2C_6H_3COCl$	ν_1=37,145		[114]. Cl^{35}. ν_3 & ν_6 refer
	ν_2=37,038		to group COCl
	ν_3=35,923	77	
	ν_4=35,834		
	ν_5=31,086		
	ν_6=31,039		
$2,4\text{-}Cl_2C_6H_3COOH$	37,432	77	[53]. Cl^{35}
	35,528		
$3,4\text{-}Cl_2C_6H_3COOH$	37,298	77	[53]. Cl^{35}
	36,576		
$o\text{-}ClC_6H_4NCO$	34,415	196	[46]. Cl^{35}
$m\text{-}ClC_6H_4NCO$	34,653	196	[46]. Cl^{35}
$p\text{-}FC_6H_4CCl_3$	39,056		[118]. Cl^{35}
	38,772	77	
	36,968		
$4\text{-}Cl\text{-}3\text{-}NO_2\text{-}C_6H_3COOH$	37,843	77	[53]. Cl^{35}
$o\text{-}ClC_6H_4CF_3$	35,633	196	[46]. Cl^{35}
$m\text{-}ClC_6H_4CF_3$	35,073	77	[46]. Cl^{35}
	34,632	196	
$C_6H_5CCl_3$	38,898		[114]. Cl^{35}; crystallographic
	38,824		splitting (two molecules in
	38,786		a common position)
	38,713	77	
	38,702		
	38,288		
C_6H_5COCl	29,03	77	[118]. Cl^{35}
$p\text{-}ClC_6H_4CHO$	34,623	77	[46]. Cl^{35}
	34,607		
$o\text{-}ClC_6H_4COOH$	36,3049	77	[126]. Cl^{35}
$m\text{-}ClC_6H_4COOH$	35,227	77	[46]. Cl^{35}
$p\text{-}ClC_6H_4COOH$	34,673	77	[46]. Cl^{35}
$5\text{-}Cl\text{-}2\text{-}OH\text{-}C_6H_3CHO$	34,968	77	[53]. Cl^{35}
$p\text{-}ClC_6H_4CH_2Cl$	ν_1=34,303		[46]. Cl^{35}; ν_1 refers to chlorine
	ν_2=32,804	196	atom in benzene ring; ν_2 to chlorine atom in methyl group
$2,4\text{-}Cl_2C_6H_3OCH_3$	36,256	77	[53]. Cl^{35}
	35,734		
$4,6\text{-}Cl_2\text{-}3\text{-}OH\text{-}C_6H_2CH_3$	35,450	77	[53]. Cl^{35}
	34,749		
$2\text{-}Cl\text{-}6\text{-}NO_2\text{-}C_6H_3CH_3$	35,219	77	[53]. Cl^{35}
$p\text{-}NO_2C_6H_4CH_2Cl$	34,311	77	[120]. Cl^{35}
$4\text{-}Cl\text{-}3\text{-}CH_3\text{-}2\text{-}NO_2\text{-}C_6H_2OH$	35,660	77	[53]. Cl^{35}
$C_6H_5CH_2Cl$	33,630	77	[46, 54]. Cl^{35}
$p\text{-}ClC_6H_4OCH_3$	34,753	77	[46]. Cl^{35}
$4\text{-}Cl\text{-}3\text{-}CH_3OH\text{-}C_6H_3\text{-}1$	34,887	77	[53]. Cl^{35}
	34,535		
$5\text{-}Cl\text{-}2\text{-}CH_3O\text{-}C_6H_3NH_2$	34,220	77	[53]. Cl^{35}
$p\text{-}ClC_6H_4COCH_2Br$	34,8224	77	[126]. Cl^{35}
$p\text{-}ClC_6H_4CH_2CN$	34,634	77	[53]. Cl^{35}
	34,593		
$p\text{-}ClC_6H_4COCH_3$	34,618	77	[46]. Cl^{35}
$p\text{-}ClC_6H_4NHCOCH_3$	34,792	77	[53]. Cl^{35}
$2,4\text{-}Cl_2C_6H_3OC_2H_5$	36,108	77	[53]. Cl^{35}
	35,406		
$p\text{-}ClC_6H_4OC_2H_5$	34,381	77	[46]. Cl^{35}
$4\text{-}Cl\text{-}3,5\text{-}(CH_3)_2\text{-}C_6H_2OH$	34,415	77	[126,129]. Cl^{35}
	34,348		

TABLE 1 (continued)

1	2	3	4
4,7-$Cl_2C_9H_5N$	35,591		[123]. Cl^{35}
	35,179	77	
	34,764		
6-ClC_9H_6N	34,628	77	[44,123]. Cl^{35}
7-ClC_9H_6N	34,681	86	[44]. Cl^{35}
2-ClC_9H_6N	33,271	77	[44,123]. Cl^{35}
2,4-Cl_2-3-CH_3-C_9H_4N	35,627	86	[44]. Cl^{35}
	34,268		
2-Cl-C_9H_6N.HCl	37,145	77	[123]. Cl^{35}
p-ClC_6H_4CH=$CHCOOH$	34,227	196	[46]. Cl^{35}
$ClOC(CH_2)_8COCl$	29,118	77	[114]. Cl^{35}
2,3-Cl_2-1,4-O_2-$C_{10}H_4$	37,114	77	[51]. Cl^{35}
1,2,3,4-$Cl_4C_{10}H_8$	36,783		[120]. Cl^{35}
	36,100	77	
	35,262		
	.....		
5-C_6H_5-4,6-Cl_2-2-CH_3-1,3-N_2C_5	35,248	86	[44]. Cl^{35}
4,6-Cl_2-2-CH_3-5-C_6H_5-1,3-N_2C_4	35,248	86	[44]. Cl^{35}
$Cl_3CCH(C_6H_4Cl)_2$	ν_1=39,039		[114]. Cl^{35}. $\nu_1-\nu_3$ due to three chlorine atoms in the trichloromethyl group, and ν_4 and ν_5 to chlorine atoms in the benzene rings
	ν_2=38,814		
	ν_3=38,487	77	
	ν_4=34,977		
	ν_5=34,868		
	Group Cl — Si		
$HSiCl_3$	19,30	4	[54]. Cl^{35}
$SiCl_4$	20,464		[54]. Cl^{35}
	20,415	77	
	20,408		
	20,273		
$C_2H_5SiCl_3$	18,756		[132]. Cl^{35}
	18,842	300	
	18,865		
	Group Cl — Ti		
$TiCl_2$	4,17	297	[135]. Cl^{35}
$TiCl_3$	7,39	297	[135]. Cl^{35}
$TiCl_4$	5,922		[136]. Cl^{35}
	5,963	243	
	5,988		
	6,022		
	6,082	77	
	6,150		
	Group Cl — Ge		
$GeCl_4$	25,746		[54]. Cl^{35}
	25,736	77	
	25,714		
	25,451		
	Group Cl — Sn		
$SnCl_4$	24,294		[54]. Cl^{35}
	24,226	77	
	24,140		
	23,719		
	Group Cl — N		
$(CH_2CO)_2NCl$	54,100	77	[133]. Cl^{35}
p-OC_6H_4NCl	44,992	77	[133]. Cl^{35}
	Group Cl — V		
VCl_3	9,40	297	[135]. Cl^{35}
	Group Cl — P		
PCl_3	26,202	77	[54,110]. Cl^{35}
	26,107		
$POCl_3$	ν_1=28,9835	77	[38,54,110] ν_1 & ν_2 refer to Cl^{35}, ν_3 and ν_4 to Cl^{37}
	ν_2=28,9378		
	ν_3=22,8432		
	ν_4=22,8067		

TABLE 1 (continued)

1	2	3	4
$POCl_2F$	29,272 28,715	20	[54]. Cl^{35}
PCl_5	32,630 32,384 32,282	77	[110,118]. Cl^{35}
$(PNCl_2)_3$	27,630 27,704 27,834 27,903	287	[110,137,138]. Cl^{35}
$(PNCl_2)_4$	27,265 28,124 28,182 28,616	287	[137,138]. Cl^{35}
	Group Cl — As		
$AsCl_3$	25,406 25,058 24,960	77	[54, 100]. Cl^{35}
	Group Cl — Sb		
SbCl	ν_1=20,90767 ν_2=19,30468 ν_3=16,47790 ν_4=15,21522	77	[8, 54, 100, 105]. ν_1 and ν_2 refer to Cl^{35}; ν_3 & ν_4 — Cl^{37}
$SbCl_5$	ν_1, ν_2=30,4 ν_3=28,3 ν_4, ν_5, ν_6=27,88	77	[118]. Cl^{35}. ν_1 & ν_2 — is a partially allowed doublet; ν_3 is a single line; ν_4, ν_5 and ν_6 is a partially allowed triplet
	Group Cl — Bi		
$BiCl_3$	ν_1=15,849 ν_2=19,531 ν_3=12,498 ν_4=15,387	83	[107]. ν_1 and ν_2 refer to Cl^{35}, ν_3 & ν_4 — Cl^{37}
	Group Cl — O		
$NaClO_2 \cdot xH_2O$	53,33	77	[139]. Cl^{35}
$AgClO_2$	54,08	297	[139]. Cl^{35}. Calculation similar to that in [43] gave asymmetry parameter η=73%.
$NaClO_3$	ν_1=30,63017 ν_2=24,14228	77	[112]. ν_1 refers to Cl^{35}, ν_2 — to Cl^{37}
$KClO_3$	28,954	77	[39, 112, 137] Cl^{35}
$Cu(ClO_3)_2 \cdot 6H_2O$	30,064	77	[114]. Cl^{35}
$AgClO_3$	29,421	77	[112]. Cl^{35}
$Mg(ClO_3)_2 \cdot H_2O$	29,885	77	[114]. Cl^{35}
$Ca(ClO_3)_2$	29,6	290	[140]. Cl^{35}
$Sr(ClO_3)_2$	29,869	77	[114]. Cl^{35}
$Ba(ClO_3)_2 \cdot 6H_2O$	29,922	77	[121, 122]. Cl^{35}
$Zn(ClO_3)_2 \cdot H_2O$	30,026	77	[122]. Cl^{35}
$Ni(ClO_3)_2 \cdot 6H_2O$	30,572	77	[112]. Cl^{35}
	Group Cl—S		
$(SNCl)_3$	29,8	285	[110]. Cl^{35}
$SOCl_2$	ν_1=32,0908 ν_2=31,8874 ν_3=25,2935 ν_4=25,1331	77	[54, 110, 111]. ν_1 & ν_2 are due to Cl^{35}, ν_3 & ν_4 — Cl^{37}
SO_2Cl_2	37,822 37,613	77	[110, 114]. Cl^{35}
$C_2H_5SO_2Cl$	32,5190	77	[126]. Cl^{35}
$CH_3(CH_2)_3SO_2Cl$	32,7592	77	[126]. Cl^{35}
$SCH=CHCH=CSO_2Cl$ | ——— |	33,1507	77	[126]. Cl^{35}
$C_6H_5SO_2Cl$	32,8920 32,5380 32,4700	77	[118, 126]. Cl^{35}
$p\text{-}ClC_6H_4SO_2Cl$	35,967	77	[120]. Cl^{35}, NQR frequency of Cl^{35} in the benzene ring also given

TABLE 1 (continued)

1	2	3	4
$2,5\text{-}Cl_2C_6H_3SO_2Cl$	37,3200		[126] Cl^{35}
	36,3913	77	
	34,4484		
$p\text{-}BrC_6H_4SO_2Cl$	32,895	77	[120]. Cl^{35}
$m\text{-}NO_2C_6H_4SO_2Cl$	32,832	77	[120]. Cl^{35}
	32,337		
$p\text{-}NO_2C_6H_4SO_2Cl$	33,438	77	[120]. Cl^{35}
$p\text{-}CH_3C_6N_4SO_2Cl$	32,460	77	[118]. Cl^{35}
$2,5\text{-}(CH_3)_2C_6H_3SO_2Cl$	32,7579		[126]. Cl^{35}
	32,5269	77	
	32,3178		
	32,2698		
	Group Cl — Cr		
$CrCl_2$	8,52	297	[135]. Cl^{35}
$CrCl_3$	ν_1=12,812	297	[135]. Cl^{35}. Intensity ratio $A_1:A_2=2:1$
	ν_2=12,848		
	Group Cl — Se		
$SeCl_4$	36,794		[114]. Cl^{35}
	36,171		
	35,696		
	35,041	77	
	34,685		
	34,534		
	Group Cl—W		
WCl_6	10,172	77	[136]. Cl^{35}
	Group Cl—F		
ClF	70,700	20	[54]. Cl^{35}
ClF_3	ν_1 = 75,1295		[54]. ν_1 refers to Cl^{35}, ν_2—Cl^{37}
	ν_2 = 59,2147	77	
	Group Cl—Cl		
Cl_2	ν_1 = 54,2475		[33, 54], ν_1 refers to Cl^{35},
	ν_2 = 42,7544	77	ν_2 — Cl^{37}
	Group Cl—I		
$\alpha\text{-}ICl$	37,185	293	[141]. Cl^{35}
$\beta\text{-}ICl$	37,202	77	[114]. Cl^{35}
$ICl_3(I_2Cl_6)$	35,680	77	[114]. Cl^{35}
	33,916		
$KICl_2$	19,6272	298,09	[142]. Cl^{35}
	19,0018	298,11	
	18,7645	298,10	
	18,4077	298,10	
$KICl_2\cdot H_2O$	18,81	296	[142, 143]. Cl^{35}
	19,2070	77	
$CsICl_2$	19,8611	299	[142]. Cl^{35}
	20,0895	77	
PCl_4ICl_2	18,94	293	[143]. Cl^{35}
NH_4ICl_2	26,14	294	[143]. Cl^{35}
$C_6H_5NHICl_2$	17,62	293	[143]. Cl^{35}
$N(CH_3)_4ICl_2$	19,35	295	[143]. Cl^{35}
$NaICl_4\cdot 2H_2O$	23,2656		[142]. Cl^{35}
	22,8844	298	
	22,1758		
	20,5916		
	23,8274		
	23,2509	77	
	22,6561		
	20,0100		
$KICl_4$	22,38	296	[142, 143]. Cl^{35}
	22,6039	77	
$KICl_4\cdot H_2O$	20,14		[143]. Cl^{35}
	24,86	296	
	28,17		
	20,3508		[142]. Cl^{35}
	25,0128	77	
	28,5004		

TABLE 1 (continued)

1	2	3	4
$RbICl_4$	22,3904	298	[142]. Cl^{35}
	22,5726	77	
$CsICl_4$	22,5911	298	[142]. Cl^{35}
	22,1991		
	22,8951	77	
	22,6256		
NH_4ICl_4	22,23	295	[143]. Cl^{35}
$NH_4ICl_4 \cdot H_2O$	19,98		[143]. Cl^{35}
	24,68	296	
	27,96		
$C_5H_5NHICl_4$	22,38	294	[143]. Cl^{35}
	XIV. Br^{79-81}		
	Group Br—Hg		
$HgBr_2$	155,47		[144]. Br^{79}
	156,65	90	
	Group Br—B		
BBr_3	ν_1=175,293	Room	[40]. ν_1 & ν_2 refer to Br^{79}, ν_3 & ν_4 — Br^{81}; η=45%; eQ= =340
	ν_2=175,264		
	ν_3=146,434		
	ν_4=146,411		
	Group Br—Al		
$AlBr_3(Al_2Br_6)$	ν_1=81,815		[145]. ν_1, ν_2 & ν_3 refer to Br^{81}, ν_4, ν_5 & ν_6 — Br^{79}
	ν_2=95,055		
	ν_3=96,426	77	
	ν_4=97,945		
	ν_5=113,790		
	ν_6=115,450		
	Group Br—Ga		
$GaBr_3(Ga_2Br_6)$	ν_1=100,795		[89]. Lines $\nu_1 \div \nu_6$ refer to Br^{81}, $\nu_7+\nu_{11}$—Br^{79}
	ν_2=100,840		
	ν_3=140,660		
	ν_4=140,700		
	ν_5=140,790		
	ν_6=140,845	77	
	ν_7=120,602		
	ν_8=120,635		
	ν_9=168,375		
	ν_{10}=168,430		
	ν_{11}=168,560		
	.....		
	Group Br—In		
$InBr_3(In_2Br_6)$	ν_1=86,912		[89] ν_1—ν_3 refer to Br^{81}, ν_4—ν_6—Br^{79}
	ν_2=106,974		
	ν_3=107,428	77	
	ν_4=104,112		
	ν_5=128,110		
	ν_6=128,608		
	Group Br—C		
CF_3Br	252,263	77	[147]. Br^{81}
CF_2Br_2	251,624	77	[147]. Br^{81}
	255,681		
$CFBr_3$	256,592	77	[147]. Br^{81}
	262,371		
CBr_4	Several lines from 265 to 268 Mc/sec	77	[95, 146]. Br^{81}
$CHBr_3$	250,527		[147, 148]. Br^{81}
	250,666	77	
	251,970		
CH_2Br_2	234,805	77	[146, 147]. Br^{81}
	235,601		
CH_3Br	220,981	77	[147]. Br^{81}
CH_3COBr	181,350		[48]. Br^{81}
	180,140		
	179,536	77	
	178,082		
$BrCH_2COOH$	286,72		48]. Br^{79}
	284,55	77	

TABLE 1 (continued)

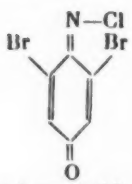
1	2	3	4
$BrCH_2CH_2Br$	216,827 218,977	77	[23, 146, 147]. Br^{81}
C_6H_5Br	207,790	77	[146—148]. Br^{81}
C_6H_7Br	210,277	77	[147, 148]. Br^{81}
$p\text{-}CH_3(CH_2)_2CH_2Br$	ν_1=249,96 ν_2=208,86	90	[148]. ν_1 refers to Br^{79}, ν_2 — Br^{81}
$3,5\text{-}Br_2C_5H_3N$	278,005	77	[123]. Br^{79}
$2\text{-}BrC_5H_4N$	265,213	77	[123]. Br^{79}
C_6Br_6	255,553 255,060 254,975	77	[50]. Br^{81}
$C_6O_3Br_4$	298,974 298,400	77	[149]. Br^{79}
	246,736 246,174	77	[133]. Br^{81}
$2,6\text{-}Br_2\text{-}4\text{-}NO_2\text{-}C_6H_2ONa$	270,32 270,71	298,5	[150]. Br^{79}
$1,2,3,5\text{-}Br_4C_6H_2$	236,042 242,176 242,767 244,949 246,140 249,314	77	[49, 50] Br^{81}
$1,2,4,5\text{-}Br_4C_6H_2$	242,75 242,00	77	[49]. Br^{81}
$2,4\text{-}(NO_2)_2C_6H_3Br$	ν_1=301,270 ν_2=251,690	77	[49] ν_1 refers to Br^{79}, ν_2— Br^{81}
$2,6\text{-}Br_2\text{-}4\text{-}NO_2\text{-}C_6H_2OH$	280,47 281,16 294,24 294,80	296,9 296,9 297,3 297,3	[150]. Br^{79}
$2,5\text{-}Br_2C_6H_3NO_2$	307,1 287,2	83	[146]. Br^{79}. Measurements with a resonance wavemeter, i.e., of low precision
$1,2,4\text{-}Br_3C_6H_3$	240,67 239,47 236,37 232,34	77	[49]. Br^{81}
$1,3,5\text{-}Br_3C_6H_3$	234,52 234,11 233,14	77	[49, 146]. Br^{81}
$2,4,6\text{-}Br_3C_6H_2OH$	275,96 277,17 284,40	297,3	[140]. Br^{79}
$o\text{-}BrC_6H_4NO_2$	300,3	83	[146]. Br^{79}. Measurements with a resonance wavemeter; error may reach several Mc /sec
$m\text{-}BrC_6H_4NO_2$	284, 4	83	[146]. Br^{79}. Measurements with a resonance wavemeter, i.e., of low precision
$p\text{-}BrC_6H_4NO_2$	274,84 284,0	299 83	[150]. Br^{79}
$o\text{-}Br_2C_6H_4$	236,068 235,969	77	[50]. Br^{81}
$p\text{-}Br_2C_6H_4$	226,49 271,125	77	[49]. ν_1 refers to Br^{81}; ν_2 — Br^{79}; [32]. η=5%
$2,6\text{-}Br_2\text{-}4\text{-}NO_2\text{-}C_6H_2NH_2$	282,458	77	[149]. Br^{79}

TABLE 1 (continued)

1	2	3	4
$2,4,6\text{-}Br_3C_6H_2NH_2$	ν_1=233,56		$\nu_1 - \nu_3$ refer to Br^{81} [49];
	ν_2=230,75	77	$\nu_4 - \nu_6 - Br^{79}$ [150]
	ν_3=230,10		
	ν_4=276,00		
	ν_5=272,68	296,8	
	ν_6=272,29		
C_6H_5Br	ν_1=224,61		[49, 148, 151]. ν_1 refers to
	ν_2=268,856	77	Br^{81}, $\nu_2 - Br^{79}$
$o\text{-}BrC_6H_4OH$	275,884	77	[48]. Br^{79}
$m\text{-}BrC_6H_4OH$	272,745	77	[48]. Br^{79}
	271,420		
$p\text{-}BrC_6H_4OH$	ν_1=269,683		[49, 147, 150, 154] ν_1 & ν_2
	ν_2=268,222		refer to Br^{79}, ν_3& ν_4—
	ν_3=225,30	77	Br^{81}
	ν_4=224,08		
$o\text{-}BrC_6H_4NH_2$	220,26	77	[49, 152]. Br^{81}
$m\text{-}BrC_6H_4NH_2$	222,61	77	[49. 152]. Br^{81}
$p\text{-}BrC_6H_4NH_2$	ν_1=265,525	77	ν_1 refers to Br^{79} [149],
	ν_2=221,86		$\nu_2 - Br^{81}$ [49]. See also
			[146, 150, 151]
$2,6\text{-}Br_2\text{-}4\text{-}NH_2\text{-}C_6H_2OH$	274,79	297,7	[150]. Br^{79}
	277,80		
$2\text{-}Br\text{-}3\text{-}NO_2\text{-}C_6H_3COOH$	302,54	296,7	[150]. Br^{79}
C_6H_5COBr	191,868	77	[48]. Br^{81}
$o\text{-}BrC_6H_4COOH$	280,66	298	[20]. Br^{79}
$m\text{-}BrC_6H_4COOH$	269,23	298	[150]. Br^{79}
$p\text{-}BrC_6H_4COOH$	280,08	297,8	[150]. Br^{79}
$2\text{-}OH\text{-}5\text{-}Br\text{-}C_6H_3COOH$	ν_1=271,820		[48]. ν_1 refers to Br^{79},
	ν_2=227,08	77	$\nu_2 - Br^{81}$
$2,4,6\text{-}Br_3C_6H_2OCH_3$	ν_1=289,194		$\nu_1 - \nu_3$— Br^{79} [49, 150]
	ν_2=283,888	77	$\nu_4 - \nu_6 - Br^{81}$
	ν_3=280,632		
	ν_4=285,800		
	ν_5=279,980	299	
	ν_6=277,255		
$o\text{-}BrC_6H_4OCH_3$	233,25	77	[49]. Br^{81}
$p\text{-}BrC_6H_4OCH_3$	226,69	77	[49]. Br^{81}
$2\text{-}CH_3\text{-}4\text{-}BrC_6H_3NH_2$	ν_1=263,616	77	[49]. ν_1 refers to Br^{79},
	ν_2=220,23		$\nu_2 - Br^{81}$
$2\text{-}Br\text{-}4\text{-}CH_3C_6H_3NH_2$	265,974	77	[48]. Br^{79}
	263,222		
$p\text{-}BrC_6H_4COCH_3$	230,37	77	[49] Br^{81}
$m\text{-}BrC_6H_4COOCH_3$	ν_1=271,772	77	[49]. ν_1 refers to Br^{79}, ν_2—
	ν_2=227,04		Br^{81}
$p\text{-}BrC_6H_4COOCH_3$	ν_1=275,960	77	[49], $\nu_1 - Br^{79}$, $\nu_2 - Br^{81}$
	ν_2=230,54		
$p\text{-}BrC_6H_4NH\ (COCH_3)$	226,80	77	[49]. Br^{81}
$p\text{-}(BrCH_2)_2C_6H_4$	257,697	77	[149]. Br^{79}
$p\text{-}(BrCH_2)\ C_6H_4CH_3$	254,290	77	[49]. Br^{79}
$2\text{-}Br\text{-}4\text{-}CH_3C_6H_3CH_3$	263,332	77	[48]. Br^{79}
$p\text{-}BrC_6H_4OC_2H_5$	266,818	77	[48]. Br^{79}
$p\text{-}BrC_6H_4N\ (CH_3)_2$	254,20		[150]. Br^{79}
	255,10	299	
	256,03		
$3\text{-}BrC_9H_6N$	275,187	77	[133]. Br^{79}
$5,7\text{—}Br_2\text{—}C_9H_6N\text{—}8\text{—}OH$	282,676	77	[51]. Br^{79}
	279,960		
$1,6\text{-}Br_2\text{—}2\text{-}OH\text{—}C_{10}H_5$	267,87	299	[150]. Br^{79}
	265,15		
$\alpha\text{-}C_{10}H_7Br$	267,895	77	[44]. Br^{79}
$p\text{-}BrC_6H_4N\ (C_2H_5)_2$	263,444	77	[48]. Br^{79}
	262,906		
$4,4'\text{-}BrC_6H_4C_6H_4Br$	271,835		[49, 147]. Br^{9}
	271,110	77	
	269,461		
	267,439		

TABLE 1 (continued)

1	2	3	4
p-$BrC_6H_4(C_6H_5)$	268,70	298,7	[150]. Br^{79}
p-$BrC_6H_4OC_6H_5$	272,500	77	[48]. Br^{79}
2,4,6-$Br_3C_6H_2SO_2C_6H_4$-CH_3-4′	ν_1=297,06		[150]. Br^{79}
	ν_2=288,40	297,3	
	ν_3=281,12		
9,10-$Br_2C_{14}H_8$	ν_1=275,053		[49], [150]. ν_1 & ν_2 refer
	ν_2=272,975	77	to Br^{79}
	271,59	297,5	
$C_6H_5CH=CBrCOC_6H_5$	276,30	297,8	[150]. Br^{79}
	Group Br — Si		
$SiBr_4$	147,576	77	[95]. Br^{81}
	147,511		
	Group Br — Ti		
$TiBr_4$	47,127	77	[136]. Br
	46,309		
	Group Br — Ge		
$GeBr_4$	175,949	77	[95]. Br^{81}
	175,584		
	Group Br — Sn		
$SnBr_4$	165,270		[23, 95, 148]. Br^{81}
	165,401	77	
	165,208		
	162,032		
	Group Br — P		
PBr_3	ν_1=220,575		[148, 153]. ν_1 & ν_3 refer
	ν_2=218,635	83	to Br^{79}, ν_3 & ν_4 — Br^{81}
	ν_3=184,257		
	ν_4=182,636		
	Group Br — As		
$AsBr_3$	173,143		[97, 104]. Br^{81}
	172,728	77	
	171,480		
	Group Br — Sb		
$SbBr_3$	ν_1=171,576		[95, 100, 153] ν_1 — ν_3 refer
	ν_2=164,768		to Br^{79}, ν_4 — ν_6 — Br^{81}
	ν_3=164,492	77	
	ν_4=143,324		
	ν_5=137,630		
	ν_6=137,403		
	Group Br — O		
$LiBrO_3$	184,12	293	[154]. Br^{79}
$NaBrO_3$	ν_1=178,95	293	[95, 154]. ν_1 — Br^{79}, ν_2 — Br^{81}
	ν_2=151,909	77	
$KBrO_3$	ν_1=173,11	293	[95, 154]. ν_1 — Br^{79}
	ν_2=149,361	77	ν_2 — Br^{81}
$CsBrO_3$	ν_1=142,735	296,9	[95]. ν_1 — Br^{81}
	ν_2=145,662	77	ν_2 — Br^{79}
$Cu(BrO_3)_2 \cdot 6H_2O$	175,70	285	[154]. Br^{79}
$AgBrO_3$	168,19	293	[154]. Br^{79}
$Mg(BrO_3)_2 \cdot H_2O$	176,60	293	[23, 154] Br^{79}
$Ca(BrO_3)_2 \cdot H_2O$	176,85	293	[154]. Br^{79}
$Sr(BrO_3)_2 \cdot H_2O$	175,25	293	[154]. Br^{79}
$Ba(BrO_3)_2 \cdot H_2O$	173,69	293	[154]. Br^{79}
$Zn(BrO_3)_2 \cdot 6H_2O$	177,38	285	[154]. Br^{79}
$Cd(BrO_3)_2 \cdot H_2O$	174,71	290	[154]. Br^{79}
$HgBrO_3$	168,91	285	[154]. Br^{79}
$Hg(BrO_3)_2$	170,78	285	[154]. Br^{79}
	172,62		
$Pb(BrO_3)_2 \cdot H_2O$	174,30	285	[154]. Br^{79}
$Co(BrO_3)_2 \cdot H_2O$	176,92	290	[154]. Br^{79}
$Ni(BrO_3)_2 \cdot 6H_2O$	177,62	290	[154]. Br^{79}
	Group Br — Cr		
$CrBr_3$	85,73	297	[135]. Br^{81}
	Group Br — Br		
Br_2	ν_1=382,04		[155]. ν_1 — Br^{79}, ν_2 — Br^{81}
	ν_2=319,03	83	$\eta = 20\%$ at 253°K

TABLE 1 (continued)

Substance	NQR frequencies, Mc/sec: transition $\pm 1/2 \rightarrow \pm 3/2$	NQR frequencies, Mc/sec: transition $\pm 3/2 \rightarrow \pm 5/2$	Temp. °K	Literature sources and other data (eqQ, Mc/sec)
1	2	3	4	5
	XV I^{127}			
	Group I — Hg			
K_2HgI_4	148,49 129,30 123,46		293 296	[144]
	Group I — B			
BI_3 (I_2I_6)	212,6	340,1	196	[22]. $\eta = 45{,}6\%$, $eqQ = 1176$. Both lines are doublets with 25 ± 5 kcs splitting
	Group I — Al			
AlI_3 (Al_2I_6)	$\nu_1 = 112{,}314$ $\nu_2 = 131{,}371$ $\nu_3 = 131{,}844$	$\nu_1 = 215{,}614$ $\nu_2 = 263{,}228$ $\nu_3 = 263{,}920$	77	[156]. $\eta_1 = 18{,}1\%$, $\eta_2 = \eta_3 = 0$, $(eqQ)_1 = 723{,}38$; $(eqQ)_2 = 876{,}52$ $(eqQ)_3 = 879{,}33$
	Group I — Ga			
GaI_3 (Ga_2I_6)	$\nu_1 = 135{,}719$ $\nu_2 = 176{,}496$ $\nu_3 = 177{,}438$	$\nu_1 = 253{,}347$ $\nu_2 = 352{,}948$ $\nu_3 = 354{,}519$	77	[156] $\eta_1 = 23{,}7\%$, $\eta_2 = 0{,}9\%$ $\eta_3 = 2{,}8\%$; $(eqQ)_1 = 853{,}92$, $(eqQ)_2 = 1176$, $(eqQ)_3 = 1186{,}91$
	Group I — In			
InI_3 (In_2I_6)	$\nu_1 = \ldots$ $\nu_2 = 176{,}763$ $\nu_3 = 177{,}146$ $\nu_4 = 122{,}728$ $\nu_5 = 173{,}177$ $\nu_6 = 173{,}633$	$\nu_1 = \ldots$ $\nu_2 = 353{,}466$ $\nu_3 = 354{,}580$ $\nu_4 = 229{,}190$ $\nu_5 = 346{,}289$ $\nu_6 = 347{,}234$	77 297	[150, 156] $\eta_4 = 23{,}7\%$, $\eta_5 = 1{,}1\%$, $\eta_6 = 0$; $(eqQ)_4 = 772{,}25$, $(eqQ)_5 = 1154{,}33$, $(eqQ)_6 = 1157{,}46$
	Group I — C			
CF_3I	310,375		83	[153]
CI_4	319,549		77	[153]
$CHI_3 \cdot 3S_8$	307,10	613,949	77	[153]. $\eta = 1{,}82\%$
CH_2I_2	286,883	568,362	77	[146, 147, 153] $\eta = 2{,}71\%$
CH_3I	265,102	529,670	77	[20, 146, 147, 151, 153] $\eta = 2{,}8\%$
trans -ICH=CHI	277,1	553,82	83	[20] $\eta = 2{,}3\%$
CH_3CHI_2	260,29		90	[78]
C_2H_5I	247,374		77	[146, 147]
ICH_2CH_2COOH	260,9		90	[151]. Measurements with a resonance wavemeter, i.e., of low precision
C_3H_7I	250,962		77	[146]
$(CH_3)_2CHI$	235,921		77	[146]
o-$C_5H_4I_2$	286,923 286,285 285,531 284,036		77	[56]

TABLE 1 (continued)

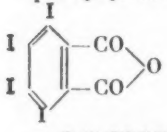
1	2	3	4	5
$mC_6H_4I_2$	286,3		83	[146]. Measurements with a resonance wavemeter, i.e., with a low precision
$p\text{-}C_6H_4I_2$	ν_1=280,147		77	[56, 95, 146].
	ν_2=275,89	ν_2=550,16		η_2=4,77% and
	ν_3=276,31	ν_3=551,68	301	η_3=3,65%
$o\text{-}IC_6H_4NO_2$	ν_1=315,19	ν_1=613,88		[150]. η_1=14,47%
	ν_2=315,97	ν_2=615,26	299,8	and η_2=14,57%
$m\text{-}IC_6H_4NO_2$	ν_1=285,63	ν_1=570,29		[150, 151].
	ν_2=286,66	ν_2=571,43	300	η_1=5,05% & η_2=3,65%
$p\text{-}IC_6H_4NO_2$	284,36	565,82	300,7	[150]. η=6,30%
C_6H_5I	274,465		77	[147, 150]
	274,978			
$o\text{-}IC_6H_4OH$	277,60	551,80	298,7	[150.] η=6,91%
$p\text{-}IC_6H_4OH$	278,1		83	[146]. Measurements with a resonance wavemeter, i.e., of low precision
$C_6H_5IO_2$	ν_1=162,23	ν_1=311,70	294	[150]. η_1=17,89%
	. . . . .	ν_2=293,30	301,4	
$o\text{-}IC_6H_4NH_2$	270,0		83	[147]. Measurements with a resonance wavemeter, i.e., of low precision
$p\text{-}IC_6H_4NH_2$	ν_1=264,280		77	[146, 149, 150].
	ν_2=261,14	ν_2=521,25	300,7	η_2=3,91%
$p\text{-}IC_6H_4NH_2\cdot HCl$	288,28	572,15	296	[150]. η=7,71%
$2,5\text{-}I_2C_6H_3CF_3$	287,2		83	[146]. Measurements with a resonance wavemeter, i.e., of low precision
$o\text{-}IC_6H_4COONa$	294,81		296,3	[150]
$m\text{-}IC_6H_4COONa$	ν_1=272,73	ν_1=545,17	298	[150]
	ν_2=273,76	ν_2=547,42		η_1=2,03% & η_2=1,27%
$p\text{-}IC_6H_4COONa$	277,59			[150]
	280,82		295,7	
	282,25			
$3,5\text{-}I_2\text{-}2\text{-}OH\text{-}C_6H_2$ COOH	295,14		296,6	[150]
	284,19			
$o\text{-}IC_6H_4COOH$	294,58	573,43	300,2	[150]
				η=14,62%
$m\text{-}IC_6H_4COOH$	275,67	548,56	301	[150].
				η=6,27%
$p\text{-}IC_6H_4COOH$	272,89	544,18	300,1	[150]. η=4,76%
	313,63	Three lines		
	316,20	about 604,	301,8	[150].
	324,03	609, and 616		
	328,53			
$m\text{-}C_6H_4COOCH_3$	276,24	550,16	297	[150]. η=5,71%
$p\text{-}IC_6H_4COOCH_3$	284,03	564,21	297	[150]. η=7,26%
$p\text{-}IC_6H_4NHCOCH_3$	273,74	546,06	301,2	[150]. η=4,49%
$p\text{-}IC_6H_4C_6H_5$	275,40		300,4	[150].
	Group I – Si			
SiI_4	ν_1=199,999	ν_1=399,993	77	[153].
	ν_2=198,736	ν_2=397,430		η_1=0,33% & η_2=0,91%
	Group I – Ge			
GeI_4	ν_1=225,088	ν_1=450,173	77	[153].
	ν_2=222,672	ν_2=445,294		η_1=0,224% & η_2=0,93%

TABLE 1 (continued)

1	2	3	4	5
	Group I – Sn			
SnI_4	ν_1=209,133 ν_2=207,683	ν_1=418,257 ν_2=415,320	77	[153]. η_1=0,4% & η_2=0,92%. see also [20, 23, 95, 100]
$SnI_4 \cdot 2S_8$	ν_1=210,746 ν_2=207,458	ν_1=420,675 ν_2=414,907	77	[100]. η_1=3,9%, η_2=0,2% $(eqQ)_1$=1402,68 $(eqQ)_2$=1383,03
$SnI_4 \cdot 4S_8$	ν_1=204,64 ν_2=205,25 ν_3=210,99 ν_4=219,04	ν_1=409,35 ν_2=410,50 ν_3=421,40	77	[100]. $\eta_1=\eta_2$=0, η_3= 3%, η_4=?, $(eqQ)_1$=1364,3, $(eqQ)_2$=1368,3 $(eqQ)_3$=1405,0, $(eqQ)_4$=?
	Group I – As			
AsI_3	207,023	395,979	77	[100, 101]. η=18,91% & eqQ=1330,23
$AsI_3 \cdot 3S_8$	227,543	455,059	77	[100, 153]. η=0,7%; eqQ=1516,86
	Group I – Sb			
SbI_3	174,356	254,637	77	[95, 97, 100, 103] η=56,5%; eqQ=895,83
$SbI_3 \cdot 3S_8$	184,151	367,023	77	[100, 153]. η=3%; eqQ=1226,26
	Group I – Bi			
BiI_3	111,320	201,380	77	[103]. η=29%; eqQ=682
	Group I – O			
HIO_3	203,12	330,84	77	[112, 150, 160]. eqQ=1141,0 η = 43,37%. A forbidden $\pm 1/2 \rightarrow \pm 3/2$ transition was observed; its frequency was 528, 746 Mc/sec (297°K)
KIO_3	ν_1=144,37 ν_2=144,91 ν_3=145,38	ν_1=288,82 ν_2=289,85 ν_3=290,71	299	[150, 157]. $\eta_1 \leqslant 0{,}02\%$, $\eta_2 \leqslant 0{,}08\%$ and $\eta_3 \leqslant 0{,}08\%$
$Ca(IO_3)_2 \cdot 6H_2O$	150,75 150,97	297,470 298,709 307,612	297	[90]
	Group I – Cl			
I_2Cl_6	458,19	909,37	77	[20, 24, 158]. η=7,72%; eqQ=3034,9
$KICl_2$	469,160 462,060		298	[158].
$KICl_2 \cdot H_2O$	471,051		298	[158].
$RbICl_2$	463,988		298	[158].
$CsICl_2$	464,949		298	[158].
$NaICl_4 \cdot 2H_2O$	461,702		298	[158].

TABLE 1 (continued)

1	2	3	4	5
$KICl_4$	477,506		298	[158].
$KICl_4 \cdot H_2O$	458,863		298	[158].
$RbICl_4$	470,617		298	[158].
	458,988			
$CsICl_4$	453,123		298	[158].
	Group I —I			
NH_4I_3	366,23	732,13	298	[24]. Doublet line with splitting of several kcs; η = 1,8%; eqQ=2440,6
I_2	332,4	644,8	293	[20]. η=15%; eqQ = 2153
	XVI. Co^{59}			
	Group Co—C			
$[C_5H_5CoC_5H_5]$ $[ClO_4]$	ν_1= . . .			[159]. $\eta \approx 0$. Presumed that ν_3 & ν_6 correspond to transition $\pm 3/2 \rightarrow \pm \pm 5/2$, & ν_3, ν_4 — to transition $\pm 5/2 \rightarrow \pm 7/2$
	ν_2= . . .			
	ν_3=24,08			
	ν_4=24,50			
	ν_5=36,12			
	ν_6=36,74		77	

Randall, Molton, and Ard [61] showed that polar factors cannot be responsible for the observed decrease of NQR frequency even in irradiated ionic crystals. This shows, once again, that consideration of geometric factors must play an important, if not the decisive role in analysis of the influence of ionizing radiation on quadrupole resonance.

The interesting fact that the rate of phase transition is retarded sharply in p-dichlorobenzene after irradiation by soft γ-rays has been reported [72]. Rate of phase transition is calculated on the change in the NQR lines for the appropriate α- and β-phases. The retardation of phase transition under the influence of radiation indicates that fairly large voids must be present in the lattice for transition to take place; it is difficult to imagine any other mechanism in which filling of the voids in a crystal with radiolysis products can influence rearrangement of the undamaged regions of the lattice.

Fig. 11. NQR signals of Cl^{35} from the α- and β-phases in 0.8 g of p-dichlorobenzene. The distance between the peaks corresponds to 26.4 kc/sec. The frequency decreases from left to right.

Studies of solid solutions [61-70] occupy an important position among the applications of quadrupole resonance. Monfils [65] was the first to propose that the influence of an impurity molecule in a solid solution on the NQR signal should be characterized by the number N of neighboring molecules of the principal substance which are brought out of resonance by the impurity molecule. At low impurity concentrations it may be assumed that N is a property of the impurity molecule in the given lattice, and is independent of the concentration. It is then easy to show [68] that the signal intensity decreases with increasing impurity concentration c, as follows

$$A = A_0 \, e^{-Nc}, \qquad (6)$$

where A_0 is the amplitude of the signal for the pure substance. Three types of A—c relationships are observed in practice [68] (Fig. 12). Curve 1 is characteristic for unlimited solubility in the given range of concentrations c; Curve 2 indicates limited solubility, and Curve 3 represents the case when the form and dimensions of the impurity molecule prevent formation of a solid solution. It was shown [64,67] that the decrease in the amplitude of the NQR signal is a consequence of the corresponding broadening of the line for the solid solution [see Eq. (3)].

Baer and Dean [70] measured shifts of NQR frequencies in impurity molecules. Their published data are very interesting and merit further study. Fedin and Kitaigorodskii [68] used a very precise method to demonstrate the absence of appreciable shifts of NQR frequencies for molecules of the main substance in solid solutions of a number of compounds in p-dichlorobenzene. They also attempted to use data of organic crystal chemistry for

TABLE 2

List of Substances for Which NQR Signals Could Not be Detected

Substance	Atom	Search band Mc/sec	Temp., °K	Literature
$CHBrI_2$	Br^{81-79}, I^{127}	-	83	[146]
$BrCH_2 — CHBr_2$	Br^{81-79}	—	83	[146]
$Br_2CH — CHBr_2$	Br^{81-79}	—	83	[146]
CH_3CH_2COCl	Cl^{35}	27—31	77	[114]
$CH_3(CH_2)_4COCl$	Cl^{35}	24—36	77	[114]
$CH_3(CH_2)_6COCl$	Cl^{35}	25—36	77	[114]
$CH_3(CH_2)_7COCl$	Cl^{35}	24—36	77	[114]
$CH_3(CH_2)_{10}COCl$	Cl^{35}	24—40	77	[114]
$CH_3(CH_2)_{12}COCl$	Cl^{35}	24—36	77	[114]
$CH_3(CH_2)_{14}COCl$	Cl^{35}	24—36	77	[114]
$(CH_3)_2CHCH_2COCl$	Cl^{35}	24—36	77	[114]
$(CH_3)_2CH(CH_2)_2COCl$	Cl^{35}	24—36	77	[114]
$CH_3CH_2CH(C_2H_5)COCl$	Cl^{35}	25—35	77	[114]
$C_6H_5CH_2COCl$	Cl^{35}	24—36	77	[114]
$C_6H_5(CH_2)_2COCl$	Cl^{36}	25—35	77	[114]
$C_6H_5CCH_2COCl$	Cl^{35}	24—36	77	[114]
α-$C_6H_5OCH(CH_3)COCl$	Cl^{35}	24—36	77	[114]
m-$NO_2C_6H_4COCl$	Cl^{35}	27—40	77	[114]
-$NO_2C_6H_4COCl$	Cl^{35}	27—40	77	[115]
p,5-$(NO_2)_2C_6H_4COCl$	Cl^{35}	27—40	77	[115]
3-ClC_6H_4COCl	Cl^{35}	27—40	77	[115]
o3,4-$Cl_2C_6H_3COCl$	Cl^{35}	24—36	77	[115]
m-BrC_6H_4COCl	Cl^{35}	28—40	77	[115]
$CH_3OC_6H_5COCl$	Cl^{35}	24—36	77	[115]
o-$C_2H_5OC_6H_4COCl$	Cl^{35}	24—40	77	[115]
p-$C_2H_5OC_6H_4COCl$	Cl^{35}	27—40	77	[115]
p-$CH_3(CH_2)_4OC_6H_4COCl$	Cl^{35}	27—40	77	[115]
$(C_6H_5)_2NCOCl$	Cl^{35}	27—40	77	[115]
$CH_3CH—CHCOCl$	Cl^{35}	24—36	77	[115]
α-$C_{10}H_7COCl$	Cl^{35}	24—36	77	[115]
2-NH_2-4-Cl-6-CH_3-$C_4H_2N_2$	Cl^{35}	33—39	77	[115]
		31—36	300	
2-NH_2-4,6-Cl_2-5-CH_3-$C_4H_2N_2$	Cl^{35}	33—39	77	
		33—37	300	[134]
2-NH_2-5-Cl-4-HOOC-$C_4H_2N_2$	Cl^{35}	34—39	77	
		33—39	300	[134]
$RbICl_2$	Cl^{35}	16—29	77	[142]
		14—39	298	
m-$Br_2C_6H_4$	Br^{81-79}	—	83	[147]
o-$BrC_6H_4CH_3$	Br^{81-79}	—	83	[147]
m-$BrC_6H_4CH_3$	Br^{81-79}	—	83	[147]
p-$BrC_6H_4CH_3$	Br^{81-79}	—	83	[147]
o-BrC_6H_4I	Br^{81-79}; I^{127}		83	[147]
p-BrC_6H_4I	Br^{81-79}; I^{127}		83	[147]
		200—340	300	[150]
m-BrC_6H_4Cl	Br^{81-79}	—	83	[147]
p-BrC_6H_4Cl	Br^{81-79}	—	83	[147]
2-Br-6-CH_3O-$C_{10}H_6$	Br^{81-79}	200—330	300	[150]
2-Br-6-OH-$C_{10}H_6$	Br^{81-79}	190—320	300	[147]
1-Br-2-OH-$C_{10}H_6$	Br^{81-79}	200—320	300	[150]
1,2-$(CH_3)_2C_6Br_4$	Br^{81-79}	230—300	77	[149]
1,3-$(CH_3)_2C_6Br_4$	Br^{81-79}	230—300	77	[149]
o-$IC_6H_4CH_3$	I^{127}	—	83	[147]
p-$IC_6H_4CH_3$	I^{127}	—	83	[147]
		215—350	300	[150]
p-IC_6H_4Cl	I^{127}	—	83	[147]
		220—370	300	[150]
2,4,6-$I_3C_6H_2COOH$	I^{127}	230—340	300	[150]
2,3,5-$I_3C_6H_2COOH$	I^{127}	240—360	300	[150]
3,5-I_2-4-OH-C_6H_2COOH	I^{127}	240—360	300	[150]
2-NH_2-3,5-I_2-C_6H_2COOH	I^{127}	240—346	300	[150]
o-IC_6H_4COOH	I^{127}	195—360	300	[150]
$(CH_2)_6N_4 \cdot C_2H_5$	I^{127}	200—340	300	[150]
$(C_6H_5)_3N \cdot HI$	I^{127}	155—340	300	[150]

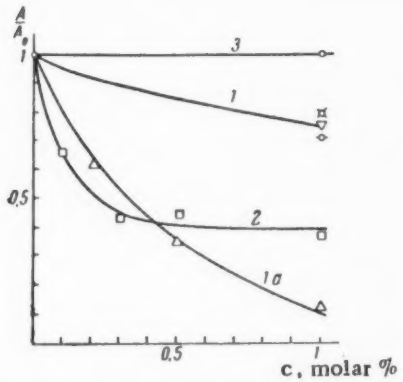


Fig. 12. Variation of the NQR signal amplitude with the impurity concentration in p-dichlorobenzene. Curve 1) unlimited solubility: a) impurity molecule larger than main molecule; b) impurity molecule smaller than main molecule. Curve 2) limited solubility; Curve 3) no solubility.

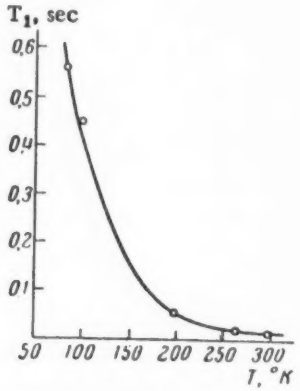


Fig. 13. Variation of T_1 in p-dichlorobenzene with temperature.

predicting values of N for several systems, with the assumption that decrease of A in a solid solution is due to statistical deformations of the lattice. This assumption was based on the results of measurements of the spin–lattice relaxation time T_1 in a solid solution [66], which show that T_1 is independent of c. At the same time, according to Hirai [73], T_1 is independent very strongly of the temperature (Fig. 13). Therefore, it may be assumed that in the first approximation the lattice dynamics remains unchanged at low c. This is also indicated by the absence of frequency shifts in the molecules of the main substance. It then follows from an analysis of the experimental data that deformation of the lattice around each impurity molecule diminishes with increasing distance from that molecule. It is possible to derive numerical characteristics for this decrease of deformation; with their aid, and on the basis of existing data on the dimensions of the impurity molecules and the molecules of the main substance [58], it is possible to predict the dimensions of the deformation region which arises when one molecule of the main substance is replaced by the impurity. The agreement with experimental data is quite satisfactory. It must be pointed out that the calculations can be completed only with the hypothesis that the size of the atoms involved in the intermolecular contacts is proportional to the variations of the corresponding interatomic distances. The interesting question of the meaning of this hypothesis and of the generality of the proportionality factor uses, which was taken as close to unity in the first calculations, requires additional study. For this it will be necessary to examine the difficulties involved in applying to analysis of crystallographic splitting of NQR lines the relationship established in [68] between the relative change of frequency $\Delta\nu/\nu$ and the relative scatter $\Delta r/r$ of the intermolecular distances in the crystal:

$$\Delta\nu/\nu = -3\Delta r/r. \qquad (7)$$

The effects of mechanical and thermal treatments of the specimens on intensity of quadrupole resonance lines have been studied in [8, 66, 68]. Dreyfus [69] observed that the NQR signal was stronger in certain solid solutions than in the corresponding pure specimens; this was explained [68] by the effect of strong overheating of the melt on the dimensions of the mosaic blocks in the crystal.

Investigations of the influence of the pressure applied to the specimen on NQR frequencies [74-76] are important. Certain conclusions drawn from these experiments were discussed in Part I, Section 6. In studies of the effect of temperature on NQR frequencies, the variations of lattice constants with temperature must be taken into account. An extensive field for investigations of intermolecular interaction in crystals is also offered by frequency shifts under the influence of pressure.

Influence of Thermal Vibrations on NQR. Because of the exceptionally strong influence of temperature of the specimen on NQR frequency (see Part I, Section 6), quadrupole resonance is a fairly sensitive indicator of thermal vibrations in a crystal. The work of Dodgen, Ragle, and Anderson [77-79] and of Skripov and Grechishkin [80] is the most significant with respect to applications of this property of NQR. The influence of reorientation about the Cl–Cl axis on the breadth of the NQR line in 1,2-dichloroethane was studied [77]. Increase of the amplitude and frequency of orientation resulted in an eightfold broadening of the line when the temperature was raised from 77°K to 154°K. The observed anomalous frequency shift was attributed by Ragle to transition to random reorientation of 1,2-dichloroethane molecules at a frequency $>10^8$ sec^{-1}. It must be emphasized that the

occurrence of such motion must indicate a phase transition into the gaseous crystalline state; i.e., it must be accompanied by an abrupt change in the breadth of the proton resonance line. Since Ragle did not detect any such change, his interpretation of the temperature–frequency relationship for 1,2-dichloroethane must be regarded as debatable. However, a similar interpretation for changes in the NQR spectrum of 1,2-dibromoethane is offered by Dodgen and Anderson [79], who attribute the transition from a two-component to a one-component spectrum at −24° to the occurrence of rapid reorientation of the molecules about the Br–Br axis. Skripov and Grechishkin [80] investigated the average life of the rotational oscillation quanta in a number of compounds [80]. They also considered the origin of the partial rotation of hexachloroethane, trichloroacetic acid, and chloral hydrate molecules; the rotating molecule was considered as a defect in the crystal lattice.

The combined influence of lattice disorder and thermal vibrations makes it impossible to observe NQR in many cases, because of excessive broadening of the resonance line. Unsuccessful attempts to detect quadrupole resonance have been reported by several authors. The summary of these data in Table 2 is certainly not complete. An examination of this table suggests that, for many of the compounds studied, the NQR lines are very much broadened owing to statistically random orientation of molecules in the crystals [81,82], while, in other cases, thermal motions may be an obstacle to detection of the signal. Obviously, there is a risk that any estimates of line breadths based on a total absence of an NQR signal may be inadequate or quite erroneous. The problem of the causes of the weakness of NQR signals for many substances can be finally solved only when improvements in the apparatus will make it possible to detect quadrupole resonance in at least some of these substances.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

BRIEF COMMUNICATIONS

PROTON RELAXATION IN AQUEOUS SOLUTIONS OF DIAMAGNETIC SALTS

IV. ROLE OF ION STRUCTURE

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The influence of the covalent character of complex particles of the $Me(H_2O)_x^{n-}$ type on the proton relaxation time T_1 in aqueous solutions may prove significant for understanding the structures of compounds of this type [1]. The influence of the structure of the particles formed on proton relaxation of the solution has been reliably established [2] in formation of complex paramagnetic ions. This influence is manifested in shielding of the magnetic moment of the central ion by the ligands. This effect is associated with an increase of the average distance of maximum approach between the paramagnetic ion and the protons, which weakens magnetic dipole interaction between them, and causes T_1 to increase. In this connection, we consider the situation arising in the case of diamagnetic ions capable of covalent interaction with water.

The addition of a ligand (water molecule) leads to formation of a covalent bond with a redistribution of electron density in the ion–water molecule system. According to [2], the effect of covalent bond formation on T_1 is opposite to that indicated above: T_1 decreases. Consecutive addition of a number of ligands may have the effect that the ion no longer influences T_1, as the certain magnetic moment which arises in the particle is "hidden" within it, shielded by the ligands, when the approach distance between the proton and the magnetic moment of the $Me^{n+} - OH_2$ system is considerably increased. This situation is not reached immediately; its occurrence depends on many factors (pH, radius and charge of the particular ion, electron shell structure, etc.). It is rather difficult to follow this process in a general form consecutively. We confine ourselves to the following considerations. Addition of the first two water molecules leads to a progressive increase of the effective magnetic moment μ_N; subsequently, especially after addition of the fourth molecule, this is followed by a decrease of the moment which either eliminates the influence of the ion on T_1 altogether, or makes this influence constant. In other words, this effect depends on the structure of the $Me(H_2O)_x^{n+}$ complex, because this structure determines the extent of approach between the proton and the "carriers" of paramagnetism. This can be illustrated by the example of uranyl nitrate solutions [3]. The configuration of this ion, and the dimensions of its constituents, are such that the solvent protons can give information on paramagnetism of the ion without hindrance (at least in acid solutions). On the other hand, coordination of six water molecules in the equatorial plane (passing through the uranium atom and the O–Ion–O line [4]) causes the influence of the ion on T_1 to increase [3]. This is because, with this configuration, the conditions for proton–ion approach not only remain the same with regard to accessibility of O–Ion bonds, but the equatorial Ion–OH_2 bonds are also accessible. If the water molecules were coordinated near the plane passing through the O–Ion bond, an increase of uranyl μ_N (in comparison with the value calculated from its magnetic susceptibility $\approx 1 \cdot 10^{-2}$ Bohr magneton) would be doubtful, because, under these conditions, shielding of the already small magnetic moment of the ion would be more probable. However, experimental results indicate an increase of the moment μ_N [$(7.2 \pm 0.9) \cdot 10^{-2}$ Bohr magneton]. It is significant that μ is increased more than sixfold, i.e., there is not even the slightest shielding [3].

Our investigation of the complex and intricate problem of the influence of structure on proton relaxation

has yielded the following preliminary results. If we assume that in a liquid solution any particular ion retains the principal features of its characteristic structure in a solid, then, if an ion consisting of particles which are separately diamagnetic has weak polarizational paramagnetism, its structure must determine its influence on T_1. With an "open" structure, this was demonstrated for the uranyl ion. It seems likely that MnO_4^- and CrO_4^{2-} * ions represent another case – a "closed" structure created by tetrahedral O^{2-} coordination [5]. It has been shown [6] that MnO_4^- is polarizationally paramagnetic; the same may be assumed for the chromate ion. The radii of these ions are large enough for them to exert an influence in solution on T_1 through the time of correlation of dipole interaction [1]. However, solutions of both ions have the relaxation times of pure water although, according to [3], their concentrations were high enough (saturated solutions were used) for their paramagnetism to influence proton relaxation.**

The situation is different with the dichromate ion, which has a more "open" structure than CrO_4^{2-} or MnO_4^-. It was found that its solutions had lower T_1; the molar relaxational shift [1] of the dichromate ion is 38 nominal units (same units as in [1]), and μ_N is $(6.6 \pm 0.9) \cdot 10^{-2}$ Bohr magneton.***

The above experimental facts show that studies of proton relaxation can give important, even if not exhaustive, information on the structure of certain ions and hydration complexes formed in aqueous solutions.

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THE STRUCTURES OF K_2OsNCl_5 AND $K[OsNBr_4H_2O] \cdot H_2O$

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Osmium, like all the other metals of group VIII, forms a large number of various complex compounds. They have been studied very incompletely from the point of view of crystal chemistry, but a survey of those which have been investigated shows that osmium can exist in two characteristic coordinations in complex compounds – octahedral and tetrahedral – in accordance with valence. Examples of octahedral coordination with quadrivalent and sexivalent osmium are K_2OsCl_6 [1] and $K_2OsO_2Cl_4$ [2]. Compounds with tetrahedral coordination (valence 8)

*In general, these ions may be regarded as products of proton (acid) dissociation of the corresponding hydrate complexes.

**The experimental details were as in [1]. Solutions of potassium salts were used for the measurements.

***An attempt was made to obtain the Mn^{7-} ion in compounds of a more "open" structure. This should be present in solutions of Mn_2O_7 in concentrated acids. However, because of the difficulties involved in work with the highest oxide of manganese, no success has been achieved as yet.

include osmium tetroxide OsO_4 [3,4] and $MeOsO_3N$ [5,6]. Compounds of the $MeOsO_3N$ type were studied in 1932, and it was found that they belong to the scheelite structure type; the Os – O and Os – N distances are 1.56 A. The short Os – O and Os – N distances in these compounds are not surprising, because, in all structures of the scheelite type, metal – oxygen bonds are considerably shortened, which indicates increased multiple bonding. In the OsO_3N^- ion, nitrogen statistically replaces oxygen, and, therefore, the distances found by x-ray investigation (1.56 A) are evidently intermediate between Os – O and Os – N. On the other hand, it was shown by later[3] electron-diffraction work that the Os – O distance in OsO_4 is 1.66 A, and this was later confirmed by x-ray structural studies [4].

In compounds of the types K_2OsNCl_5 and $KOsNBr_4 \cdot 2H_2O$, our attention was first focused on the presence of nitrogen atoms as ligands in them.

As long ago as 1932, Verhulst [7] attempted to investigate the structure of K_2OsNCl_5 crystals. However, the x-ray techniques of that time did not allow him to complete the investigation. He determined only the lattice constants (a = 9.06, b = 13.16, c = 7.33 A) and the space group Cmc; Z = 4. In view of the fact that, for a long time, we did not succeed in growing K_2OsNCl_5 crystals, described originally by Dufet [8], the structure studies were commenced with $KOsNBr_4 \cdot 2H_2O$. The crystals of the latter compound are of the rhombo-pyramidal symmetry type. The lattice constants were determined with the RKOP camera and modified in accordance with x-ray patterns obtained in an KFOR camera with NaCl standard: a = 9.53 ± 0.03, b = 13.363 ± 0.007, c = 7.44 ± ± 0.03 A; Z = 4. The systematic extinctions and the presence of a strong piezoeffect led to the choice of two space groups, Cmc and C2cm (Ama2). Subsequent construction of Patterson projections in the three principal directions made it possible to select the Cmc space group with certainty. Verhulst [7] found the same group in his analysis of the diffraction patterns of K_2OsNCl_5.

We eventually succeeded in growing K_2OsNCl_5 crystals; in accordance with Debye patterns and other x-ray diffraction patterns, they proved to be isostructural with $KOsNBr_4 \cdot 2H_2O$. The lattice constants of K_2OsNCl_5 were determined accurately in the KFOR camera with NaCl standard: a = 8.92 ± 0.03; b = 12.913 ± 0.007, c = 7.24 ± ± 0.03 A.

Investigations of the structure of $K_2OsNBr_4 \cdot 2H_2O$ were commenced with analysis of the P(uv) Patterson projection, whereby the coordinates of the Os, Br_I, and Br_{II} atoms were determined. The $\rho(x,y)$ electron density projection constructed from F_{exp} with signs determined from the coordinates of Os, Br_I, and Br_{II} confirmed the analysis of the Patterson projection, and gave more precise values of the $\underline{x}$ and $\underline{y}$ coordinates for Os, Br_I, and Br_{II}. At the same time, a maximum appeared on the projection; this was interpreted as corresponding to the potassium atom. Similar projections for K_2OsNCl_5 crystals made it possible to determine the $\underline{x}$ and $\underline{y}$ coordinates of the Os, Cl_I, and Cl_{II} atoms in this compound. Here, the potassium atoms occupy two fourfold positions. The $\underline{z}$ coordinates of the Os atoms and halogens in both compounds were determined from the P(uw) and P(vw) projections. The $\underline{x}$ and $\underline{z}$ coordinates of K_I, K_{II}, Cl_{III}, and N atoms in the K_2OsNCl_5 structure were determined more precisely from the difference projections $\rho_{exp} - \rho_{Os}$, $\rho_{exp} - (\rho_{Os} + \rho_{Cl_{III}})$, $\rho_{exp} - (\rho_{Os} + \rho_N)$. The $\underline{x}$ and $\underline{z}$ coordinates of K, H_2O_I, H_2O_{II} in the structure $KOsNBr_4 \cdot 2H_2O$ were found more precisely from the difference projections $\rho_{exp} - (\rho_{Os} + \rho_{H_2O_{II}})$, $\rho_{exp} - (\rho_{Os} + \rho_N)$, and confirmed by electron-density projections $\rho(xz)$ both for K_2OsNCl_5 and $KOsBr_4 \cdot 2H_2O$. The two lateral projections are both noncentrosymmetric, and phases were therefore calculated in their construction.

The investigation showed that the compounds $KOsNCl_5$ and $KOsNBr_4 \cdot 2H_2O$ are isostructural; in the outer sphere of $KOsNBr_4 \cdot 2H_2O$, H_2O occupies the place of one of the potassium ions in the K_2OsNCl_5 structure, and H_2O_{II} occupies the place of Cl_{III} in the inner sphere. Osmium has octahedral coordination in both structures. In K_2OsNCl_5, nitrogen is in the trans-position to Cl_{III}, and in $K[OsNBr_4H_2O]H_2O$ it is in the trans-position to H_2O_{II}. The Os – N distances in both structures are shortened, and are 1.61 A. The Os – Cl_{III} distance in K_2OsNCl_5 is 2.16 A, and the Os – Cl_I and Os – Cl_{II} distances are 2.40 A. Shortening of the Os – N distance was reported earlier in the structure of $MeOsO_3N$ [5,6]. According to Lewis and Wilkinson [9], the type of Os – N bonds in the compounds $KOsO_3N$ and K_2OsNCl_5 is the same. Shortening of the Os – N bond can be explained with the aid of concepts of 1σ and 2π bond formation, as was done by Syrkin and Belova [10]. The unexpected shortening of the Os – Cl_{III} bond was attributed by Volkov and Dyatkina [11] to formation of an additional δ-bond between Os and Cl_{III}.

The atomic coordinates are:

	K_2OsNCl_6			$K[OsNBr_4H_2O]\cdot H_2O$			
	x	y	z		x	y	z
Os	0	0,162	0	Os	0	0,162	0
K_I	1/2	0,184	0,058	K	1/2	0,184	0,058
K_{II}	0	0,108	0,558	H_2O_I	0	0,108	0,558
Cl_I	0,184	0,035	0,058	Br_I	0,184	0,035	0,058
Cl_{II}	0,315	0,212	0,441	Br_{II}	0,315	0,212	0,441
Cl_{III}	0	0,203	0,286	H_2O_{II}	0	0,199	0,271
N	1/2	0,368	0,286	N	1/2	0,367	0,292

Work is in progress on more precise determinations of the coordinates of the light atoms.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

CURRENT EVENTS

FIFTH INTERNATIONAL CRYSTALLOGRAPHIC CONGRESS

K. S. Aleksandrov, P. V. Klevtsov, and N. N. Neronova

Translated from Zhurnal Strukturnoi Khimii, Vol. 1, No. 4, pp. 504-507, November-December, 1960

The Fifth Congress of the International Union of Crystallography was held in Cambridge (England) from August 15 to August 24. About 1200 scientists, representing 30 countries, took part in the work of the Congress.

The Soviet Union was represented by 45 scientists from various cities. The delegation, headed by Academician N. V. Belov, included Academician A. V. Shubnikov, Corresponding Member (Academy of Sciences, USSR) G. B. Bokii, Academician of the Academy of Sciences, Belorussian SSR, N. N. Sirota, Professors G. S. Zhdanov, I. I. Shafranovskii, V. I. Iveronova, M. V. Klassen-Neklyudova, Doctor of Physical and Mathematical Sciences B. K. Vainshtein, M. I. Zakarova, and others. The Soviet delegation took part in the exhibition of books and models of crystal structures. A special issue of the journal Kristallografiya (No. 4 for 1960) was timed for the Congress. The Soviet scientists prepared 28 papers for presentation at the meetings and symposia.

Sir Lawrence Bragg gave a paper to all the participants in the Congress on the considerable growth of the potentialities of x-ray analysis. The following papers were given by eminent crystallographers at the plenary sessions: "Crystal chemistry of silicates with large cations" (N. V. Belov), "Theory of metals" (N. F. Mott, J. C. Slater, L. Pauling), "Magnetic orientation" (J. H. van Vleck), "Structure of crystalline proteins" (M. F. Perutz), and "Theory and practice of direct methods of structure analysis" (B. K. Vainshtein, A. I. Kitaigorodskii, I. M. Rumanova, and Z. V. Zvonkova).

The work of the Congress comprised 19 sections.

Most of the papers were concerned with apparatus and methods used in diffraction measurements, latest advances in methods of structure determination, and investigations of crystal structures of various substances by x-ray, electron and neutron diffraction methods.

In the apparatus section, scientists from the United States and Britain reported on new automatic diffractometers for investigations of single crystals. New recording diffractometers for work in low- and high-temperature regions have been developed in Japan. A diffractometer for work with substances of high activity has been designed in Harwell (England). R. P. Ozerov (Karpov Institute, Moscow) reported on the possibilities of neutron-diffraction studies (with relatively high resolution) of powders and single crystals with a reequipped standard GUR-3 x-ray goniometer. Most recent apparatus was demonstrated at the exhibitions of the Congress.

Considerable attention was devoted to techniques of measurement of x-ray intensities in different methods of photography. Programming of crystallographic problems for various types of computers was considered, and publication of the programs was proposed.

Meetings of the section on progress in structure determination were of considerable interest; in particular, the papers by J. Karle and H. Hauptman, who are known for their work on development of direct methods. The former gave a detailed account of the procedure of phase determination by a direct method for all space groups, and gave typical examples for centrosymmetrical and noncentrosymmetrical groups. H. Hauptman gave a paper on restandardization of structure factors. The work of I. L. Karle was concerned with application of the statistical method to determination of the structure of N-benzyldihydronicotinamide. Methods (sign relations, minimalization, Fourier transforms, optimal shift) for structure determination were discussed.

Whereas, formerly, various two-dimensional projections were generally used in structure analysis, under modern conditions the extensive use of computers makes it possible to use three-dimensional data (examples of the solution of some such problems were reported at the Congress).

Over 200 papers contained data on complete or partial determination, or refinement, of structures of minerals (including clay minerals), metals and alloys, inorganic and organic crystals, proteins, and fibrous substances. For a more economical use of the available time, and to ensure some degree of systematization of such extensive data, 10-15 papers on related subjects were presented to the various sections by a single speaker (30-45 min), and this was followed by a discussion (the Rapporteur system, used at the Fifth Congress for the first time).

The papers on minerals were mainly concerned with crystal-chemical studies of silicates. They included reports on the structure of bikitaite $LiAlS_2O_6 \cdot H_2O$ by D. Appleman (USA), harmotome by R. Sadanaga, F. Morumo, and I. Takeuchi (Japan), goderite by S. G. Fleet (England), and of other minerals. Several investigations were concerned with refinement of known structures. In particular, the work of H. Megaw et al. (England), and J. V. Smith (USA) was concerned with the ordered distribution of aluminum and silicon atoms in feldspars. It is now possible to distinguish between aluminum–oxygen and silicon–oxygen tetrahedrons, whereas it was formerly believed that aluminum and silicon are distributed statistically in silicate frameworks. G. W. Brindley and his associates dealt with methods for determination of the distribution of aluminum in clays by two types of coordination, tetragonal and octahedral. Phase transitions in minerals were investigated in detail in some of the reported researches.

Papers (about 80) on inorganic structures can be divided into five large groups:

1. Structures of binary and more complex oxides; in particular, compounds of Ti, V, and Sb.
2. Structures of salts of oxy-acids.
3. Structures of complex compounds.
4. Studies of the nature of the chemical bond in inorganic crystalline compounds.
5. Other structures.

Many papers were concerned with structure investigations of substances with magnetic and ferroelectric properties. This represents mainly the work of French (E. F. Bertaut, A. Durif, J. Dulac, et al.), and British (W. Johnson and J. A. Bland) scientists on determinations of structures of the perovskite and pyrochlore type, mainly containing rare-earth elements and titanium, vanadium, chromium, and antimony, and of the spinel and garnet types.

Swedish scientists reported on their studies of aluminum selenate (C. Johansson) and basic thorium selenate $Th(OH)_2SeO_4$ (C. Bergstrom and C. Lundgren). K. H. Jost (Germany) used direct methods for determining the structures of sodium and silver metaphosphates, based on spiral tetrahedral chains. A joint paper by A. Santoro (Italy) and S. Siegel (USA) gave the results of a study of the noncentrosymmetric structure of ammonium bromate. Studies of the structure of magnesium and calcium carbonates, H_5IO_6, $K_3V_5O_{14}$, and other salts of oxy-acids were reported.

The papers by R. Hesse (Sweden) and C. Peyronel (Italy) were concerned with dithiocarbamates. E. L. Lippert and M. R. Truter (England) reported on the structure of zinc acetylacetone with zinc in fivefold coordination. C. Panattoni and E. Frasson (Italy) showed that the structure of the complex compound of silver thiocyanate and phosphyne is based on AgSCN – AgSCN... chains. Other communications dealt with investigations of antimony trichloride (R. Hulme and J. T. Szymanskii, England), complex nickel thiocyanate (S. E. Rasmussen, Denmark), and structure and nature of bonding in carbonyl cobalt and nickel compounds with additional organic ligands (L. F. Dahl and D. L. Smith, USA).

Questions of chemical bonding in inorganic compounds were, in most cases, incorporated in experimental investigations.

About 60 of the papers presented at the Congress were concerned with results obtained in studies of the structures of organic substances.

The work of American and British scientists on determination of the structure of insulin (in particular, the

paper by D. Hodgkin et al., Oxford) was reported at the meetings of the section on proteins and related compounds. Studies of the structure of viruses and ribonuclease (globular protein) are continuing in the laboratories of Birkbeck College in London. N. S. Andreeva and V. I. Iveronova (USSR) put forward certain new principles for classification of fibrous proteins.

Several papers touched upon questions of symmetry, antisymmetry, and color symmetry. A. L. Mackay (England) reviewed the latest contributions to the theory of symmetry groups. C. Hermann (Germany) considered certain possible interpretations of color symmetry groups. Kasper (USA) reported on the application of magnetic symmetry to neutron-diffraction data, and gave examples of magnetic structures NiMn, α-Mn, Mn_3O_4 described by magnetic space groups. The communication by Academician N. V. Belov on his joint work with N. N. Neronova and the American scientists T. D. H. Donnay and C. Donnay on the compilation of tables of magnetic space groups, which will supplement the well-known International Tables in determinations of magnetic structures by neutron diffraction, aroused interest.

Twenty-five papers were presented at meetings of the section on crystal growth, morphology, and twinning. They were concerned mainly with experimental data on crystal growth, morphology, and twinning. The paper by T. A. Hoffmann (Hungary) contained a new theory of fusion and a theory of grain formation, predicting the existence of very small crystalline aggregates in the solid state. Questions concerned with the structure of the interface between a melt and a growing alkali halide crystal, growth characteristics on the surfaces on tin dendrites, growth of threadlike trioxane crystals, mechanism of the growth of sucrose crystals in solution, and x-ray studies of growth structures in alkali halide crystals grown from solution were respectively dealt with in papers by W. Zimmerman and W. Wodhan (USA), K. E. Puttick, J. H. Robertson, and H. E. C. Powers (England), and L. Johnson and P. L. Smith (USA). G. A. Bassett (England) made an attempt to confirm experimentally the origin of such characteristics of the microstructures of evaporated thin metal films as the high dislocation density (10^{10} per cm^2), different types of grain faces, etc. The film by Academician A. V. Shubnikov and V. F. Parvov, entitled "Crystal growth," which demonstrated a number of interesting, little-known and new effects in the growth of crystals, was shown at one of the meetings of the section. Professor I. I. Shafranovskii developed the theory of crystallographic forms and the morphology of twins in his paper.

A considerable number of papers at various sections of the Congress dealt with investigations of the physical properties of crystals.

The section of phase transitions was mainly concerned with communications on studies of the structure of piezo- and ferroelectric materials in various phases. In particular, the paper by R. Pepinsky et al. (USA) dealt with methods for determining absolute configurations in ferroelectric crystals. Considerable interest was aroused by the paper by Yu. N. Venevtsev, G. S. Zhdanov et al. (Karpov Institute, Moscow), entitled "Crystal chemistry of compounds of the perovskite type with special dielectric properties." The authors had carried out extensive experimental and theoretical investigations of ferroelectric materials of the ABO_3 type with a perovskite structure. Several of the compounds investigated by them are only now beginning to be studied in foreign laboratories.

A characteristic feature of the papers presented at the physical sections of the Congress was the extensive application of various methods of structure investigation to searches for causes of the anomalies in the physical properties of crystals. The most interesting papers in this context were those of B. C. Frazer (Brookhaven Laboratory, New York) on studies of various phase modifications of $NaNO_2$, precise determination of the structure of the tetragonal $BaTiO_3$ phase, and determination of the magnetic structure of $CrVO_3$ by means of neutron diffraction. Several papers were concerned with application of nuclear magnetic resonance (proton resonance, quadrupole resonance) to solution of structural and physical problems. Thus, H. E. Petch and K. Pennington (Canada) determined the positions of boron atoms in the structures of the minerals inderite and lesserite, and the electric field gradients around each of the three nonequivalent boron nuclei in their crystals, by means of quadrupole resonance of B^{11} nuclei. A group of Swiss scientists (F. Herlach et al.) used nuclear quadrupole resonance in conjunction with x-ray dielectric investigations for studying phase transitions in crystals of alkali iodates.

After the conclusion of the sectional meetings on August 20-24, two symposia were held.

Thirty-four papers were presented at the symposium on thermal motion in crystals and molecules. The introductory lecture "Interaction of mechanical and electromagnetic waves in crystals," was given by J. S. Slater (USA).

The second symposium, on the theme "Lattice defects and mechanical properties of solids," included about one hundred original communications. The introductory paper, under the same title, was read by Professor N. F. Mott (England). Most of the communications dealt with observations and explanations of the interaction of dislocations with each other and with packing errors and impurities in the lattice. The potentialities of electron microscopy for observing dislocations in thin metallic films undergoing deformation directly in the microscope were considered in several communications. Some papers also dealt with observations of dislocations in nonmetallic crystals by the etching method (P. L. Pratt and co-workers, England), and by the x-ray method (A. R. Lang, T. Sawkill et al., England) in a number of metals and alloys.

During their stay in England, the Soviet delegates had an opportunity to become acquainted with the educational system in the universities and colleges of Cambridge, Oxford, and London (in particular, with the teaching of crystallographic sciences), and to visit a number of chemical and physical laboratories in Cambridge, the laboratories of John Bernal and Kathleen Lonsdale in London, and the laboratories of D. Hodgkin and Hume-Rothery, and the computer laboratory in Oxford.

Some members of the Soviet delegation visited the Harwell Atomic Research Establishment, and also the cities of Leeds and Bristol, in order to become acquainted with the work of teaching and scientific institutions in England.

At the General Assembly of the Union, simultaneous with the Congress, P. P. Ewald (USA) was elected the new President. N. V. Belov (USSR) remains as one vice-president; the other vice-president elected was Kathleen Lonsdale (England). Soviet scientists were elected to various executive bodies of the Union of Crystallography, and to various committees: G. S. Zhdanov was elected a member of the Executive Committee, G. B. Bokii was reelected as co-editor in the Commission on "Structure Reports," M. M. Umanskii remains a member of the Committee on equipment, N. L. Smirnova was elected to the committee on crystallographic data, I. I. Shafranovskii to the committee on education, and M. A. Porai-Koshits to the committee on computation technology.

It was decided to hold the Sixth Congress in Italy (Rome) in 1963, a conference on magnetism and crystallography in 1961 in Japan, and a conference to celebrate the 50th anniversary of the discovery of x-ray diffraction in Munich in 1962.

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) } Dokl(ady) AN SSSR }	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Life Sciences: Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Life Sciences: Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
		Life Sciences: Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Chemical Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Earth Sciences: Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Earth Sciences: Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
		Mathematics: Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Physics: Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
		Physics: Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
	Élecktrosvyaz	Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Iz. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations		1 1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union		1 1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute		1 1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (In English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd		48 1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.		4 1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*		1 1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*		1 1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*		1 1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i teoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimli	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

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